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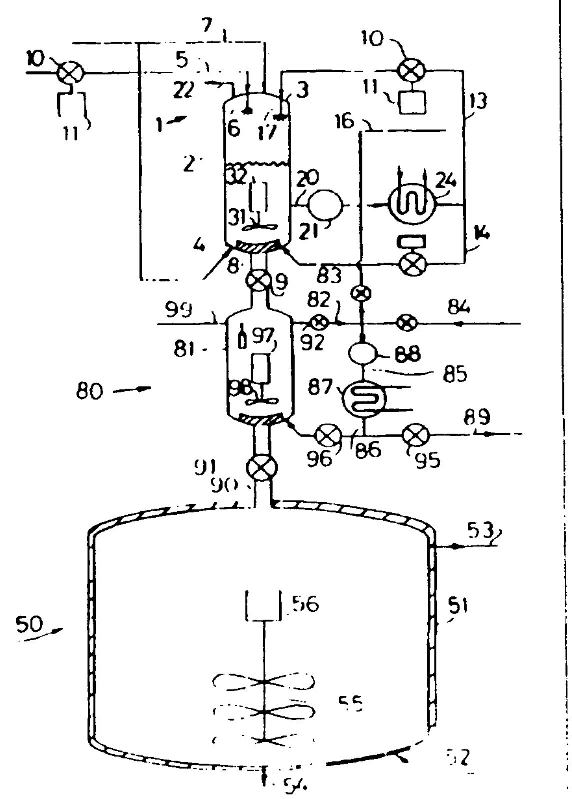
(57) Abstract

The present invention relates to a hydrocarbon product and to a method and a plant for manufacturing same. The invention in particular relates to a method and a plant for manufacturing a new hydrocarbon product in the form of a suspension; partly comprising gas hydrate particles saturated with at least one hydrocarbon and partly comprising a liquid hydrocarbon medium surrounding the gas hydrate particles, or into which the hydrate particles are suspended; and this hydrocarbon products itself. An important object of the invention is to generate hydrate under conditions controlled in such a manner that the hydrate generated is "dry", i.e. without any free water content, as all water included in the generating process has been converted into hydrate before the hydrate is collected and used in the further processing for the manufacture of the final hydrocarbon product.



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# METHOD AND PLANT FOR THE MANUFACTURE OF A HYDROCARBON-SATURATED PRODUCT AS WELL AS THE PRODUCT ITSELF.

The present invention relates to a hydrocarbon product and to a method and a plant for manufacturing same. The invention in particular relates to a method and a plant for manufacturing a new hydrocarbon product in the form of a suspension; partly comprising gas hydrate particles saturated with at least one hydrocarbon and partly comprising a liquid hydrocarbon medium surrounding the gas hydrate particles, or into which the hydrate particles are suspended; and this hydrocarbon product itself.

From Norwegian patents Nos. 149.976, 175.656 and 172.080 it is previously known to manufacture gaseous hydrate (below also referred to as gas hydrate or only hydrate) by bringing gas and water into contact with each other at suitable temperature and pressure conditions. Reference is also made to WO 93/01153 and WO 94/00713 within the same patent family as the above Norwegian patents; and further it is referred to US patent No. 2.356.407.

Previously hydrate manufacturing has taken place in the presence of an unspecified amount of water, and the result has accordingly been that "wet" hydrate has been generated, i.e. hydrate comprising relatively large amounts of free water, i.e. water not converted into hydrate during the hydrate-generating process.

Such an excess amount of water may be due to various factors, e.g. that water has been used as a cooling agent during the generating of hydrate and accordingly has been supplied in large quantities, or the reaction time i.e. the time during which water and gas has been in close contact, has been so short that not all the water in the process has been converted into hydrate. Still further problems may be that unsuitable or somewhat random pressure and/or temperature conditions have prevailed in the generating process or quite simply be that excessive amounts of water have been present during most of the generating process.

An important object of the present invention is to generate hydrate under conditions controlled in such a manner that the hydrate generated is "dry", i.e. without any free water content, as all water included in the generating process has been converted into hydrate before the hydrate is collected and used in the further processing for the manufacture of the final hydrocarbon product.

By always providing for the presence of excess hydrate-forming hydrocarbons in relation to the amount of water supplied, it is also ensured that the generated hydrate obtains a gas density close up to the maximum, theoretical limit of slightly above 180 $Sm^3$ gas per $m^3$ generated hydrate, (which is the maximum density for methane gas in gaseous hydrate). When the expression "saturated" is used in the present application, it is to indicate that the converted amount of water, i.e. the hydrate, is completely saturated by the hydrocarbons being present.

In order to generate dry hydrate it may be preferable that sufficient cooling is obtained in a different manner than by supplying cooled water only. The cool water should on the contrary be supplied to the reactor in an amount only sufficient for the generation of hydrate. In other words there should always be an excess amount of the hydrate-forming hydrocarbon(s) and never an excess amount of water during the generating process. Accordingly the generated hydrate compound has a high density of gas, a high energy content and has a reduced sintering tendency.

One object of this invention is to provide a new hydrocarbon product preferably with a high energy content, and preferably having a volume relation between the contents of gas and the contents of solid matter of at least 130 $Sm^3$ gas/$m^3$ solids.

Another object of this invention is to provide a new method for manufacturing such a hydrocarbon product reasonably in large quantities.

A further object is to provide a new plant for realizing the above method, preferably a simple, robust and

inexpensive plant which may be built up from conventional and thoroughly tested components and units.

It should be mentioned that the present application is not limited to the use of gas for generation of hydrate. Any hydrate-forming hydrocarbon or any mixture of hydrate-forming hydrocarbons may be used independently of whether the hydrocarbons are present in a gaseous or a liquid phase, or in a mixture of such phases.

The present invention also relates to how a hydrocarbon product comprising both particles of dry hydrate and a hydrocarbon medium, preferably liquid but also without any free water, may be generated. The product qualities stated above are important to obtain hydrate which may be manufactured, stored, transported and handled in large quantities.

According to the present invention the generation of hydrate from water and hydrocarbons should take place at such a high temperature that water being present, does not freeze to ice at all, or only to a very small extent, while the mixture is later cooled to a temperature below 0°C, but where this cooling down to temperatures below the freezing point of water does not take place before all the water present is converted into hydrate, and preferably after suspension of the hydrate particles in a hydrocarbon medium which together make up the end product. Thus the end product will comprise a water-free or ice-free hydrate, preferably in the form of particles, and when the particles are surrounded by a large or small amount of water-free hydrocarbon(s), preferably in liquid form, the hydrocarbon(s) will therefore act as a lubricant between the hydrate particles. This end product or suspension which during storing and transport will have a temperature below 0°C, will be much simpler to handle than a similar mixture which in addition comtains free water. The end product may be a slurry or a paste which may be transported and stored by means of previously known transport machinery and storage tanks. Accordingly, the end product may also be compacted or

further diluted with liquid hydrocarbons, and the fact that free water and ice do not exsist in the product, reduces or completely avoids the risk of sintering and generation of solids during further treatment. In addition the liquid hydrocarbon component will act as a very efficient medium for regulating the temperature within huge volumes of hydrate, both because the temperature transmission between the liquid hydrocarbons and the hydrate particles is excellent and because the liquid hydrocarbon may be separated from the hydrate particles in different ways and for different reasons, e.g. for the purpose of temperature control. Therefore both the maintaining of a low temperature e.g. -20°C in the product during transport and storing, and the heating of the product containing the hydrate when the gas which are enclosed in the hydrate is to be dissociated, are simplified.

Accordingly, it is also an object of the present invention to provide a new hydrocarbon product in which a major part of the energy content is bound in the hydrate of which the temperature may be easily controlled, and which can easily be stored, transported and dissociated as desired.

To obtain an easy understanding of how dry and wet gas hydrates act, they may be compared to dry or wet snow, as the latter compacts much more easily and sticks to all surfaces. Dry snow will obviously be much simpler to handle, transport and store than wet snow.

The presence of free, non-converted water in the hydrate or in the hydrocarbon medium will reduce the energy content, make the handling of the hydrate more difficult, and will in addition cause real problems when the hydrate compound is cooled below 0°C, as existing free water will then freeze to ice causing sintering of the compound which then may clog in the pipes and the tubes, forming a hard or lumpy material being difficult to handle.

To specify which conditions should be satisfied to ensure generation of dry hydrate, a more detailed study of

the relative amounts of materials will be made to secure an energy balance during the generating process.

To determine the required supply of cooling medium relative to the supply of hydrate-forming water, the heat-energy balance will now be considered. Generally, the heat balance over the reactor may be stated as in the following expression (enthalpi changes because of a possible pressure change in the gas is not taken into account)

$$q_{water}+q_{gas}+q_{medium}+q_{hydrate}+q_{system} = 0 \qquad (1)$$

where q represents the heat transport expressed as heat energy per unit of time, and the indexes refer to each single compound, i.e. $q_{medium}$ represents the effect from the cooling medium in the heating balance, $q_{system}$ refers to the heat transport between the reactor and the surroundings, etc. Below these references will be abbreviated to $q_v$, $q_g$, etc.

Each single term included in the heat balance (1) may be stated as a function of bulk transport, specific heat capacity and temperature differences, possibly also as enthalpi changes (for the hydrate generation) and the coefficient of thermal conductivity (for the heat transport) between the reactor tank and its environment. If, as a first approximation, it is assumed that the values of the heat capacity and the thermal conductivity are constant with respect to temperature changes, the heat balance (1) may be written as follows:

$$m_vC_v(T_v-T_d)+m_gC_g(T_g-T_d)+m_mC_m(T_m-T_d)+\Delta H_hm_h+m_hC_h(T_h-T_d)+q_s=0 \qquad (2)$$

The symbols in equation (2) has the following definitions:

$m_v, m_g$ etc. = bulk transport for each single component, positive values (represent transport) into the system and negative values out from the system.

| | | |
|---|---|---|
| $C_v, C_g$ and $C_m$ | = | specific heat capacity of water, gas and cooling medium, respectively. |
| $T_v, T_g$ and $T_m$ | = | temperatures of water, gas and cooling medium supply, respectively. |
| $T_d$ | = | average working temperature in the hydrate-generating reactor, more specifically the final temperature in the mixture of hydrate and cooling medium in the lower portion of the reactor. |
| $T_h$ | = | equilibrium temperature for generating or/dissociation of hydrate. |
| $\Delta h_h$ | = | generation-enthalpi for hydrate. |

The working temperature, $T_d$, will be somewhere between the freezing point of water (appr. 0°C) and the theoretical hydrat generating temperature, $T_h$. In many circumstances the temperature $T_d$ will, when generation of hydrate according to the present invention is of interest, be very close to the temperature in the surroundings $T_o$. The heat transport $q_s$ towards the environment will accordingly have a small value when compared to some of the other components contributing to the heat balance as expressed in equation (2).

The heat energy balance over the hydrate generator as found by equation (1) or (2), states the relations between the different variables (bulk transport and temperature of the different components). From equation (2) e.g. the following conditions for manufacturing of hydrate without free water may be found:

$$m_m \geq -\frac{m_v C_v (T_v - T_d) + m_g C_g (T_g - T_d) + \Delta H m_h + m_h C_h (T_h - T_d) + q_s}{C_m (T_m - T_d)} \qquad (3)$$

As according to this invention it is presumed that all water shall be converted into hydrate, the following equation must be satisfied

$$m_h = m_v + m_g \qquad (4)$$

The relation between gas and water in the hydrate will be defined by the socalled stuffing or packing density $\alpha$ which refers to the number of unit volumes of gas (expressed in standard cubic meter)($Sm^3$) that are incorporated in 1 cubic meter hydrate. This stuffing density $\alpha$ in general will be between 150 and 180. For natural gas the specific weight is approximately 0,735 kg/$Sm^3$ (at 15°C and 1 atmosphere) meaning that hydrate in dry condition will comprise between 110 ($\alpha$=150) and 132 ($\alpha$=180) kg for each cubic meter of hydrate. The exact amount of gas (expressed in weight units) being bound in each cubic meter of dry hydrate, should in practice be established from measurements of the stuffing density $\alpha$ obtained. The relations between the volume flow of hydrate, water and gas, determined by equation (4), therefore will be determined with a desired accuracy when one of the flows, for example the supplied amount of water, is known.

The heat exchange with the surroundings, $q_s$, will depend on several parameters such as the size of the plant, the design and materials used, and accordingly has to be calculated or determined by experiments in each single case.

In many uses of the method according to this invention, the temperature difference between the surroundings and the inner portion of said hydrate-generating reactor will be rather small and accordingly the heat transport out from or into the reactor, $q_s$, will be small related to other contributions to the heat balance, so that this contribution may be omitted in a first approximation.

The working temperature, $T_d$, generally will be slightly below the equilibrium temperature, $T_h$, for hydrate generation/desintegration, e.g. 3 or 4°C below $T_h$ at a pressure of 60 bar. Stronger cooling during the hydrate generation of course will lead to a lower working temperature. During the hydrate generation itself the working temperature should not be lowered substantially below 0°C to avoid generation of ice instead of hydrate at this step in the process. The equilibrium temperature for hydrate generation/desintegration may

be found in the literature or estimated from calculations.

Information related to the enthalpi during generation of gas hydrate from different hydrate-forming gases, may also be found in literature, calculated, or determined by experiments. For some uses it is sufficient to estimate the enthalpi for the generation process to approximately 95 kcal/kg.

The remaining terms in the expression (3) are either constants ($C_v$ etc.), temperature values ($T_v$ etc.) given from existing conditions or selectable values. A sufficient exact value of the minimum supply of cooling medium may be found from the equation (3).

The most important components in equation (3) will in many cases be $\Delta hm_h$ and $C_m(T_m-T_d)$. However, if $T_v$ and $T_g$ are below the value of $T_d$, there is reason to believe that the contribution from water and gas supply will be balanced by the contribution from the cooling of generated gas hydrate, $m_hC_h(T_h-T_d)$.

When the above premises are met the reaction described in equation (3) may be simplified to

$$m_m \geq \frac{\Delta Hm_h}{C_m(T_d-T_m)} \qquad (5)$$

The expression (5) may be used in these examples to estimate the relation between the supply of water and the supply of cooling medium calculated from the specific heat capacity of the cooling medium, $C_m$, the temperature difference between the cooling medium at the input and at the output, $T_c - T_m$, the balance between the masses (4) and the composition of the bulk gas hydrate mass as stated by the stuffing density $\alpha$. Values of the hydrate generation heat, $\Delta H$, may be found in the literature.

The following example illustrates the use of expression (5) for calculating the required supply of a cooling medium.

A condensed fraction having a specific heat capacity of

1.58 kJ/°K kg is us d as a cooling medium. The cooling medium is supplied to the hydrate-generating zone having a temperature of -35°C. The working temperature $T_d$ in the hydrate-generating zone will be approximately 10°C at a pressure of 60 bar. Calculated or obtained stuffing density is 175, which leads to a gas hydrate compound containing 175 x 0,735 = 129 kg gas/m$^3$.

The generation enthalpi for hydrate, as mentioned above, is approximately 95 kcal/kg or approximately 398 kJ/kg. Inserted for ΔH in equation (5) this gives:

$$m_m \geq \frac{398 \cdot 940}{1,58(10-(-35))} = 5.262\ kg/hour$$

when generation of 1 m$^3$ (=940 kg) gas hydrate is considered. The gas hydrate mass will contain 940-129 = 811 kg of water. The condensate at a temperature -35°C therefore has to be supplied at a rate exceeding 5262/811≈6,5 related to the amount of water, to ensure that dry hydrate is produced.

It has not been previously known how important it is that the hydrate should not include free water. Just this recognition may be taken as the basic feature of the present invention. The present invention as defined in the claims below comprises a method of producing "dry" hydrate, a method of producing a suitably composed hydrocarbon product from the dry hydrate, a plant adapted for implementing said methods and the product itself; and the invention implies all the advantages and meet all the requirements stated in the specification.

According to a preferred method the first cooling medium does not include free water and may preferably consist of liquid hydrocarbon or a liquid hydrocarbon composition, and this first cooling medium is used for direct cooling down to a temperature preferably just above 0°C during the generating process; whereupon a second cooling medium, also without any free water, is used for further cooling of the product down to a temperature well below 0 C.

The first and the second cooling mediums may be represented by the same liquid or by two different liquids.

To give a still better understanding of the present invention reference is made to the more detailed description of an embodiment of a preferred plant for manufacturing dry gas hydrate, that is hydrate without any free, converted water, and a further description of the product itself. While the function of said plant is described, this will at the same time give a description of the method according to the invention. In this connection reference is also made to the drawings in which:

Figure 1 illustrates a simple basic embodiment of the plant according to the present invention,

Figure 2 illustrates a somewhat different embodiment of the plant according to the present invention, where the hydrate-generating zone is separated in two chambers within a common container, and

Figure 3 illustrates in some more detail an implementation of a plant including some specifications in particular of the relative volumes of the throughput.

It is to be noted that the same reference numbers are used in all figures when practical. It should also be noted that the figures do not illustrate all details in the plant, but emphasize the portions of the process which are essential to understanding the present invention, without overloading the drawings. Finally it should be mentioned that the different figures and parts of same are not necessarily shown at the same scale.

Here follows a short description of the main components included in the plant as shown i Figure 1.

The plant comprises a reactor 2 with a supply pipe 5 for water and two further supply pipes 7 and 15 for one or more hydrate-forming hydrocarbons. Generally these hydrocarbons, at least partly, are supplied as a gaseous medium. All the supply lines are preferably provided with the necessary valves such as 10 and control or regulating

devices for these valves, such as 11. In close connection to the reactor 2 there is an external temperature control system including a heat exchanger 24 connected to a source 25 of cooling medium, at least one supply channel 13, 14 for said cooling medium, preferably a liquid, an outlet 20 for a cooling medium from the reactor 2, and the required pumps such as 21, valves such as 18, and control or regulating devices for these, such as 19 and similar conventional components. The parts of the plant which so far have been mentioned, make up the hydrate-generating zone 1.

Below the hydrate-generating zone 1 there is arranged a cooling zone 80 which in one hand comprises a cooling container 81 with an inlet 8 for an intermediate product produced in the reactor 2, provided with an inlet valve 9. Still further down the cooling container 81 is provided with an outlet 90 for the finished hydrocarbon product or the end product. This outlet 90 is equipped with a suitable outlet valve 91.

In connection with the cooling container 81 there is provided a further temperature controlling, external circulation loop comprising a heat exchanger 87 which is connected to a cooling medium source 79 (which may be identical to the above mentioned coooling medium source 25), and which is connected to the cooling container 81 via the outlet 82, the inlet 86, and the required pumps 88 and valves 92, 93, 94, 95, 96. The cooling medium used may be supplied from the inlet lines 16 and/or 84.

The plant still further comprises a storage tank 51 which in its upper part is provided with an inlet 90 and in its lowermost part an outlet 54. The storage tank 51 may preferably be provided with a stirring device 55 driven by a motor 56 and may in addition be connected to an external temperature control system being only indicated in the figure by means of the outlet 53 and the inlet 52; as it is implied that the substance removed from the storage tank 51 via the outlet 53 may be circulated through a heat exchanger (not shown in the figure) returning to the storage tank 51

via the inlet 52 when the required temperature has been obtained, similar to the cooling loops shown in connection with hydrate-generating zone 1 and cooling zone 80.

For an overview the process will be divided below in two steps:

STEP a:

THE GENERATING OF HYDRATE

In the plant according to Figure 1 water is led together with gas or another hydrate-forming and hydrocarbon-containing fluid, to the reactor 2 at such pressure and temperature conditions that hydrate 12 is formed, but as already mentioned, in such a manner that there will be no excess water in the tank. This may e.g. be ensured by using a control loop, whereby a detector (not shown) at the bottom of the tank 2 dilivers a control signal back to the control units 11 as soon as traces of water are detected, and the control units 11 then in turn control the setting of the valves 10. As another example there may exist predetermined limits for setting of the different valves in such a manner that water never will gather at the bottom of the tank. A first, cold, liquid cooling medium, which does not include any water, e.g. a condensate of natural gases, is supplied to the reactor 2 in a controlled amount and at a controlled temperature via the loops 16, 24, 13, 14 so that the temperature in the reactor 2 is maintained within the hydrate-forming limits related to the prevailing pressure in the reactor. The relation between the amount of water supplied at 5, the amount of cooled first cooling medium and gas as supplied at 7, is regulated or controlled as already suggested, in such a manner that all the water supplied to the reactor 2 is converted into hydrate. The first cooling medium which is heated due to the generation of hydrate, or at least a certain part of said medium, if required may be separated, e.g. by filtering, from the generated hydrate (or it may be treated together with said hydrate); is taken out of the reactor 2 at 20 and

then cooled in the external heat exchanger 24, whereupon this first cooling m dium is recirculated via the connections 13 and 14 and transported back to the reactor tank 2 to cause further cooling of the contents of the reactor tank, preferably by direct contact with the product within the tank. The hydrate 12 already at this stage of the process will consist of a particulate mixture or suspension of "dry" hydrate, i.e. hydrate without any free water, and the above mentioned first cooling medium which does not comprise water. The temperature of this mixture or this intermediate product, is somewhere between the temperature of the first cooling medium and the temperature limit or equilibrium level for hydrate generation at the prevailing pressure in the reactor tank 2. Normally the prevailing pressure during the hydrate generation will be rather high, e.g. 60 bar. And all the tanks, pipes and control components (in the generating zone) of course have to be dimensioned to endure such a high pressure.

STEP b: COOLING OF HYDRATE

When the intermediate product has been transferred to the cooling tank 80 via the connection 8 and the controllable valve 9, further cooling takes place by means of an external cooling loop 82, 88, 85, 86, 86, 96 for a second cooling medium. The first cooling medium included in the intermediate product which is generated in step a, is removed totally or partly and replaced by this still colder second cooling medium. This second, colder cooling medium preferably has such a temperature and is provided in such an amount that the hydrate is maintained stable down to one atmosphere pressure, or approximately 1 bar a. Then a second intermediate product is obtained and this comprises dry hydrate as particles and a cooled, water-free cooling medium (possibly including a mixture of the first and the second cooling medium); and this second intermediate

product is transferred via the connection 90 and the valve 91 to the storage tank 51 and is stored as cooled down, preferably at one atmospheres pressure. The volume relation between the cooling medium and the hydrate particles is maintained low, however, not so low that not a certain portion of the cooling medium may be separated from this second intermediate product for circulation and cooling. This is illustrated in Figure 1 as the storage tank 51 receives the second intermediate product via the connection 90 and the valve 91, while portions of the other cooling medium may be circulated and are temperature controlled via the outlet 53, the inlet 52 and a heat exchanger (not shown on the figure). The second cooling medium may possibly have a similar or an identical composition as the first cooling medium, such that the only difference is the working temperature. However, the two cooling media may also have different compositions. It is mentioned in particular that one or both media may comprise selected hydrate-forming components.

The process described briefly above will be explained more in detail below and then based on two different embodiments shown in Figure 1 and Figure 2, respectively.

In a basic production plant all components shown in Figure 1 may be used, such as reactor 2, cooling tank 80 and storage tank 51.

A hydrate-forming hydrocarbon (preferably substantially in gasform) is supplied to the reactor 2 through the pipe 7, while water is supplied via the pipe 5. The amount of water supplied is controlled and limited dependent on other parameters such as pressure and temperature; so that preferably all supplied water is converted into hydrate in the reactor 2. In this connection the equilibrium conditions in equations 3 and 4 above are referred to. The hydrate is formed, if the water enters and is atomized through the nozzles 6, as small, crystaline particles falling down in the tank 2, like snow flakes. Heat energy liberated during

the hydrate generation is removed by direct flushing with the first cooling medium, preferably condensate, which in a cooled condition is supplied through a line 13 and preferably also through a nozzle 17 in the reactor tank 2, and possibly also through a pipe 14 entering close to the bottom of the reactor tank 2. It should be mentioned that gas and water may be brought together in a different way, e.g. small bubbles of gas may be led through a bath of water. The essential matter is that water and gas are in direct contact with each other, and has a large common surface while a long reaction time is allowed. In both these examples the height of the tank 2 is important. The higher the tank the longer is the reaction time which may be obtained.

The heated cooling medium is drained or drawn out of the reactor tank 2 through a pipe 20, and is cooled in a heat exchanger 24 before returning to the reactor tank 2 via the tubes 13 and/or 14. The first cooling medium which is supplied to the reactor tank 2 may, if desired, include a fraction of light hydrocarbons which together with the supplied gas may be converted into hydrate when brought into contact with water.

Thus a suspension or slurry is generated comprising hydrate and also a liquid first cooling medium at the bottom of the reactor tank 2. This mixture will have a relatively high temperature, e.g. 10-15°C, but will not include any free non-converted water. To ensure that this mixture, which may be referred to as a first, intermediate product, does not include any free water, the supplied amount of water is controlled and/or limited as explained above, and possibly the supplied first cooling medium in addition incorporates some hydrate-forming components which will imply that occurring small amounts of free water also will be converted into hydrate.

When the desired amount of this intermediate product has been generated in the reactor container 2, a volume of the intermediate product is conveyed via the pipe 8 and the valve 9 out to a cooling tank 81 in the cooling zone 80. The

content of the heated, first cooling medium in this intermediate product is completely or partly substituted by a second, heavily cooled cooling medium, and this cold, second cooling medium is supplied to the cooling tank 81, (e.g. at a temperature of -10 til -20°C or possibly still lower), through a pipe 86 and a valve 96. Remaining portions of the relatively hot first cooling medium 102, will be expelled and replaced by the second, cold cooling medium and is then returned to the reactor circuit 1 via tubes and valves 92, 82, 93 and 83.

When the intermediate product has been cooled down in the cooling zone 80, it is applied via a tube 90 and a valve 91 to a storage tank 51 in which the product (which now is referred to as the end product as soon as a stable final temperature has been obtained) preferably is stored at a temperature which gives an end product being stable at atmospheric pressure and at a specified temperature e.g. -10°C or lower, possibly down to -40°C.

To avoid strong pressure pulses in the process plant, the pipes leading to and from the cooling tank 81, being the first place where a low pressure exists, are equipped with valves 92, 96 which may be closed when the valve 91 is opened.

A somewhat different embodiment of the present invention is shown in Figure 2. The method used is, however, substantially the same as already explained, but the plant itself may have a simpler design. In the plant according to Figure 2 both the generation and the cooling of the hydrate suspension is undertaken in one common tank 2'. A restriction 35 will, together with a sufficient supply of a cold second cooling medium, ensure that the lower portion (the cooling zone 80) of the reactor tank 2', all the time is filled up by a cold, second intermediate product. A sluice assembly 60, allows transmission of the hydrate compound from the high pressure zone 1 (uppermost in the reactor tank 2') to the low pressure zone in the storage tank 51 without generation and transmission of high pressure pulses within

the plant. It should be noted that the second, cold cooling medium may be supplied to the sluice assembly 65 through the pipeline 68 from a low pressure reservoir, is led out from the sluice volume 65 through the pipeline 69 and e.g. into the cooling circuit for the lower portion, i.e. the cooling zone 80 of the tank 2', via the pipeline 84.

The reactor 2' and the containers 81 and 51 can preferably be equipped with thermally insulated walls in a manner known per se.

The reactor 2' may preferably also be equipped with water detectors close to the bottom level, for detection of collected water, or may possibly be provided with a view glass for visual observation of precipitated water. Such detectors may be adapted to transmit signals for the control of valves for supplying water and/or cooled hydrocarbon medium, so that the conditions for production of water-free hydrate are maintained or re-established. An operator may possibly correct the flow rates according to the indications of water at the bottom of the reactor 2'.

Inert components, i.e. gaseous components which cannot be converted into hydrate at prevailing process conditions, as e.g. nitrogen, oxygen, rare gases, hydrogen etc., ought to be removed from the reactor 2 or 2'. As an example a minor gas flow may be led from the top 3 of the reactor 2 through an outlet 22, preferably placed close to the top of the reactor 2 or 2'.

The pipes 5, used for the supply of water and the pipes 13, 14 used for cooling medium or condensate, ought to be provided with flow control means, e.g. controllable valves 10 or pumpes having adjustable flow rates, both provided with associated control units 11, so that these flows may be controlled to obtain suitable volume relations between the water and hydrocarbon supply, preferably as stated according the above stated heating balance.

The cooling tank 81 may preferably be equipped with a thermometer or another type of temperature detector 99, generating a signal representative of the temperature in the

suspension or the mixture of hydrate and hydrocarbons in the tank, and probably also pressure detectors (not shown) for sensing the pressure, so that the signals obtained may control the filling/cooling and/or emptying of the cooling container 81 and possibly also other process steps. It may be broadly suggested that the temperature in the hydrate-generating zone 1 is approximately 2-4°C below the equilibrium temperature for generating hydrate at the prevailing pressure, which here is relatively high, e.g. 10-40 bars. The temperature in the cooling zone 80 may be -10°C or still lower, and the pressure at the same place e.g. 1 bar. In the storage tank the temperature may be still lower, e.g. down to approximately -35°C and the pressure may then be equal to the ambient pressure.

In the specification above only the basic or quite necessary components are mentioned and the relative volumes are not exactly stated.

A more precise and full description of a complete plant for cooling of hydrate by means of recirculated condensate follows below with reference to Figure 3. In connection with the description below there are included some specific values in the form of calculated examples, which only should be considered as approximate values without any limiting effects on the implementation of this invention.

In the hydrating process shown, fresh-water is used as a hydrate basis, and recirculated condensate is used as a cooling medium. Both the hydrate generation and the output of the finished product takes place continuously.

The fresh-water used may be generated by desalting of sea water in a fresh-water generator 105. The fresh-water generator 105 may itself consist of one or more sea water pumps (P100) and batteries of semipermeable diaphragms, through which the desalting takes place. The sea water is pumped until a pressure of 60 bars has been reached, before feeding it towards the diaphragms. The fresh-water leaves the system at 15 bar a.

The hydrate water is fed together with cooled and

recirculated condensate at 0°C to a plurality of containers 2 assumed to be connected in parallel (only one is shown), and these feeding flows are distributed evenly over the total volume and are contacted with the natural gas feed supplied via the pipe 7, via nozzles 6 installed in the ceiling and at the cylinder walls. The hydrate generation takes place at 60 bar a, and a suspension or slurry comprising hydrate and condensate, builds up on the bottom of the reactor 2 where the temperature is approximately 15°C, which here is the equilibrium temperature. The amount of natural gas supplied to the reactors via the input 7 is estimated to 700.000 $m^3$/day.

The condensate which takes up the heat energy dissipated during the hydrating process, is discharged from the reactors 2, cooled down from +13° - 0°C in the recirculating cooler 24 which e.g. may be connected to a propane cooling circuit 25 and then recirculated to the reactors 2. The amount of hydrating heat which has to be removed, will be approximately 21 MW. The recirculating loop is equipped with a recirculating pump 21 for condensate.

The hydrate suspension 100 representing an intermediate product, is removed from the bottom of the reactor(s) 2 and sent to a cooling container 81 where the hydrate suspension 100 is cooled down to -20°C. This cooling is provided by a cold condensate circuit 87, connected to the cooling container 81, in which filtered condensate is delivered from the cooling container at -20°C and cooled down to -30°C in the condensate circulation cooler 87, and returned to the cooling container 81. In the cooler 87 the cooling takes place by evaporation of propane at -40°C. The flow of propane is supplied to a propane cooling circuit 79 which comprises a cooling circuit compressor and a propane condensate which may be based on sea water. This cooling circuit 79 may possibly produce frost, in the shape of refridgerated propane, both to the recirculating cooler 24 and the condensate cooler 87.

The cooled suspension from the cooling container 81 is

supplied to a hydrate/condensate separator 111, from which the end product is taken out as a hydrate paste consisting of approximately 20 volume-% condensate and approximately 80 volum-% hydrate, to be stored at atmospheric pressure. The separated condensate is (at 111) mixed with the added condensate from a condensate store 106 and with recirculated condensate in the cooling loop 2, 24 for the reactor, and this mixture is supplied to the recirculating cooler 24.

In addition the plant shown in this figure comprises the following components treating the below mentioned chemicals at the conditions listed:

| | |
|---|---|
| sea water taken in (at 5) | 913 $m^3$/hour |
| gas supply (at 7) | 700.000 $Sm^3$/day |
| hydrate generator (2A) | 60 bar, 13°C |
| output of sea water (from 2A) | 1098 $m^3$/hour |
| slurry valve (from 2A) | 673 $m^3$/hour, 0°C, 15 bar |
| cooling container (81) | 15 bar |
| circulating pump (for 87) | 274 kW |
| condensate cooler (87) | 5350 kW, -20°C to -30°C |

The first intermediate product consists of hydrate particles without any free, non-converted water, suspended in a first cooling medium/carrier liquid which e.g. may consist of a condensate having traces of hydrate-forming hydrocarbons. The amount of hydrate may here e.g. be 50% of the total volume of the intermediate product. The intermediate product therefore will have a low viscosity. The end product similarly comprises hydrate particles. These particles still are suspended in a carrier liquid or in a second cooling medium. It should be noted that a second hydrocarbon medium does not include substantial amounts of hydrate-forming hydrocarbons or compositions which easily may be liberated as wax or other liquid or solid components, and of course not any free water. Finally it should be mentioned that the amount of the hydrocarbon medium relative to the amount of hydrate preferably is less in the end product than in the intermediate product, e.g. approximately 20 volume-%, so that the end product more or less has the

consistence of a paste. However, the application is not limit d to just these volume relations, however, a preferred volume relation may be 70 volume-% hydrate and 30 volume-% solid matter.

During use and storage the hydrocarbon product may be relatively solid, acting as a rather compact paste, and may in addition be further compacted to obtain an increased energy content for each volume unit.

During transport the product may possibly be diluted by adding more of the second cooling medium, and may then be still simpler to handle with pumps etc.

Moreover, the plant may be constructed in many different manners. It may e.g. include only one reactor which can work batchwise, even if larger plants are preferred, including two or more reactors 2, connected in parallel and always working in different stages of the process. For a plant with several reactor tanks running in parallel, one common or several separate parallel cooling tanks 81 may be used, even if the most natural solution is to let all the generators discharge to a common storage tank 51. The composition of the different cooling media may also be the same so that the only feature distinguishing these media from each other is the temperature. However, it is preferred that only the first cooling medium comprises hydrate-forming components while the second cooling medium preferably is completely free of hydrate-forming components. All the cooling circuits described may also be replaced by corresponding conventional cooling circuits of other types.

The method, the plant and the product according to the present invention may be used in different industrial processes. Thus the invention may be used for converting a natural gas into a hydrocarbon product which may be stored and transported under conditions being simple to obtain from a technical point of view. The method may accordingly be used in connection with production and transporting of natural gas from primary gas fields, and in particular from remote gas fields to terminals arranged close to the user or

the market. Fluids from so-called associated gas fields, i.e. oil fields which in addition to the hydrocarbon liquid (oil) comprises greater or smaller amounts of gas components, may of course also be converted into hydrocarbon products of the kind mentioned above. The converting of such gas may then also represent a profitable oil and gas production, in particular from small and remote oil and gas fields.

Further this invention may be used where it is a need for taking care of and store volatile hydrocarbon components for a shorter or longer time period. Such needs may in particular exist at locations where an excess amount of gas is present in association with oil production locations and oil refining plants, in connection with loading, unloading and transporting of crude oil, for collecting volatile components (VOC) from the crude oil, for loading of refined products as petrol, diesel oil etc.

The product according to this invention may be used for different purposes, e.g. as a medium for storing and transporting natural gas, as fuel for energy producing machines or in heating plants, and as a source for natural gas components and light hydrocarbon liquid components which may be treated and refined in different manners in chemical plants. It may in particular be suitable to use the product as fuel for vessels e.g. as an environmental conserving fuel for ferries.

The plant according to the invention may be installed on vessels or platforms offshore or may be built as stationary plants on land.

In order to further explain what is shown in Figure 3, the following is remarked, whereby Figure 3 in the following text is described from the inlet to the plant at the upper left part of the figure, to the outlet from the plant at the lower righthand part of the figure.

The two inlets shown to freshwater generator 105 indicate that the freshwater generator in the first place has an inlet for seawater, which typically can be 913 $m^3/h$ or

0,254 $m^3/s$. These and other magnitudes in the following description however, are only meant to be examples of typical values. The other input to freshwater generator 105 indicates that it also needs a supply of electric power, and the power consumption is stipulated to be 2355 KW. The freshwater flowing out of freshwater generator 105 will then be present at a pressure of about 15 bar and in an amount estimated to be 138 $m^3/h$. This freshwater passes through a pump denoted P-100 which can increase the water pressure by 40 bar and this pump will then have a power consumption of 219 KW. The hydrate water being led into the reactor(s) 2A, 2B and so forth through supply pipe 5 typically has a temperature of 15°C. The pressure in the hydrate-generating reactor 2A, 2B is typically 60 bar, whereby the gas flowing in through supply pipe 7 and nozzles 6 are supplied to the oil and gas processing plant in an amount estimated to about 700,000 $Sm^3$/day.

From supply pipe 13 condensate at about 0°C flows into the reactor(s) and this comes from the resirculation cooler 24 which may have a cooling requirement of about 21 MW and the cooling circuit 25 preferably can be a propane cooling circuit having a power consumption somewhat above 4 MW. The pump P-104 supplies cooling water from a seawater source in an amount of about 4,000 $m^3/h$ and with a power consumption of about 790 KW. The seawater leaves the propane cooling circuit 25 through outlet UT.

Some of the cooling water from the seawater inlet is passed from pump P-104 to another propane cooling circuit 79 which has a power consumption of about 2 MW. The amount of seawater flowing thereto can be about 1,000 $m^3/h$. It is to be noted however, that propane cooling circuits are referred to here only as an example of cooling circuits, since all conventional cooling circuits can be employed as long as the capacity is sufficient. This will also be seen from the application as a whole. The object is here that the circulation cooler 87 shall be able to deliver condensate at a temperature of about -30 C into the upper inlet to cooling

tank 81. The condensate being here used for cooling comes from a condensate/hydrate slurry being formed in generator 2 underneath the hydrate layer 12 and being introduced into cooling tank 81 through the lower inlet therein, at at temperature of about 15°C.

The plant also uses condensate from a condensate storage 106 in an amount of about 40 $m^3/h$, and this condensate is lead through pump 102 and pump 101, also denoted 21 i Figure 3, to the resirculation cooler 24. An intermediate product in the form of a slurry at a temperature of about -20°C and a pressure of about 60 bar is discharged at the bottom of cooling tank 81 and is conveyed to a hydrate/condensate separator 111 which in part direct condensate back into the system through pump P-105 and in part conveys the hydrate product, which can typically be in paste form, out through outlet 53 for storage and transport.

Moreover in Figure 3 there are included necessary pumps and valves in order that the plant shall be able to operate.

# C L A I M S

1. A method for manufacturing a hydrocarbon product comprising a hydrate of at least one hydrate-generating hydrocarbon, wherein

a) the hydrate-forming hydrocarbons and water are brought together in a hydrate-generating zone (1) at hydrate-generating pressure and temperature conditions,

c h a r a c t e r i z e d in that

the heat energy liberated during the generation of hydrate is removed by means of a first liquid and anhydrous cooling medium which is brought to flow through the hydrate-generating zone (1) in such quantities and at a first temperature ($T=T_1$) being so low that hydrate is generated, but not being so low that frozen water is generated in an irreversible manner in more than insignificant quantities; the relative quantities of the supplied water and the supplied first cooling medium being set so that substantially all water is converted into hydrate; thereby generating a first intermediate product comprising hydrate particles of a hydrocarbon saturated hydrate substantially free from water and ice and surrounded by or suspended in the first cooling medium, and that

b) an anhydrous and liquid second cooling medium is added to the first intermediate product in a cooling zone (80) at a second temperature ($T=T_2$) lower than the freezing temperature of water, to cool the first intermediate product further down to obtain an end product comprising particles of anhydrous, saturated gas hydrate surrounded by or suspended in the first and/or the second cooling medium, whereupon the end product is pressure released and removed from the cooling zone (80).

2. Method according to claim 1,

c h a r a c t e r i z e d in that the partial pressure of the hydrate-forming hydrocarbons in the hydrate-generating zone (1) is above 15 bars, preferably above 30 bars; and

that the average temp rature in the hydrate-generating zone (1) is maintained at a level which at a minimum is 2°C preferably approximately 4°C below the equilibrium temperature for generating/dissociating of hydrate at the present partial pressure of the hydrate-forming hydrocarbons, but above the freezing point of water.

3. A method according to claim 1 or 2, characterized in that the supplied amount of hydrate-forming hydrocarbons is maintained in excess related to the supplied amount of water in the hydrate-generating zone (1) during the complete generating process in the generating zone (1).

4. A method according to claim 1, 2 or 3, characterized in that the second cooling medium is supplied to the cooling zone (80) in such a quantity and at such a temperature ($T=T_2$) that the hydrate is cooled down to a temperature ($T=T_3$) at which the hydrate (12,101) is stable at a pressure corresponding to the surrounding air pressure.

5. A method according to one of the claims 1-4, characterized in that the steps a) and b) take place in separated pressure containers (2,81; Figure 1).

6. A method according to one of the claims 1-4, characterized in that the steps a) and b) are performed consecutively in one and the same pressure tank (2',81').

7. A method according to one of the claims 1-6, characterized in that the end product (103) after the completion of st ps a) and b), is introduced into a pressure sluice (60) adapted for transport of the end product to a storage tank (51) having a pressure below the working pressure in the cooling zone (80), preferably

approximately 1 atmosphere.

8. A method according to claim 7, c h a r a c t e r i z e d in that the steps a) and b) are carried out in a unitary pressure container (2, Figure 2) which is divided in two parts and is provided with a narrow passage (35) between the hydrate-generating zone (1) and the cooling zone (80), restricting exchange/transport of cooling medium between the two zones.

9. A method according to one of the claims 1-8, c h a r a c t e r i z e d in that at least some portions of the second cooling medium is separated from the hydrate and sent to further cooling e.g. in an external heat exchanger (87) whereupon the cooled, second cooling medium is partly circulated back to the cooling zone (80), and is partly supplied to or allowed to flow into and mix with the first cooling medium in the hydrate-generating zone (1).

10. A method according to one of the claims 1-9, c h a r a c t e r i z e d in that the hydrate-generating hydrocarbons comprise hydrocarbon components included in natural gas and in particular in methane.

11. A method according to one of the claims 1-10, c h a r a c t e r i z e d in that the first cooling medium comprises hydrate-forming hydrocarbons.

12. A method according to one of the claims 1-11, c h a r a c t e r i z e d in that the cooling of the second intermediate product in step b) is carried out in the presence of hydrate-forming hydrocarbons until the temperature in the hydrate compound has reached a level lower than the freezing point of water, preferably a temperature at which the hydrate is stable.

13. A method according to one of the claims 1-12, c h a r a c t e r i z e d in that destabilizing amounts of volatile components present in the hydrate compound when it has been cooled down to a temperature at which the hydrate is substantially stable, is removed so that an end product is obtained in which the hydrocarbon carrier medium has a gas pressure which at the final temperature is below the final pressure.

14. A method according to one of the claims 1-13, c h a r a c t e r i z e d in that the portion of hydrocarbons not forming hydrate, in the first and/or in the second cooling medium, does not at all contain or contains only insignificant amounts of components which will settle as wax or another solid or high viscous material at the lowest temperature in the process.

15. A method according to claim 14, c h a r a c t e r i z e d in that the portion of non-hydrate-forming hydrocarbons in the first and/or the second cooling medium, substantially is made up of a $C_5$ to $C_{10}$-petroleum fraction, preferably a condensate fraction.

16. A method according to one of the claims 1-15, c h a r a c t e r i z e d in that water and/or the hydrate-forming hydrocarbons and the first cooling medium is supplied to the hydrate-generating zone (1) through separate atomizing nozzles (6,17).

17. A plant for manufacturing a hydrocarbon product, which plant comprises

- means (7) adapted for supplying hydrate-forming hydrocarbons,
- means (5,6) adapt d for supplying water, and
- means (13,14,17) adapted for supplying and possibly recirculating a first cooling medium,

c h a r a c t e r i z e d in that the plant is divided

into

1) a hydrate-generating zone (1) which is connected to the above means, and

- means (10) adapted for controlling the relation between the amount of water supplied and the supplied amounts of the first cooling medium so that all or a substatial part of the water will be converted into hydrate (12) when hydrate-forming hydrocarbons and water are brought together in the hydrate-generating zone (1) at hydrate-generating conditions, and
- control means adapted to control a first temperature within the hydrate-generating zone (1) so that it corresponds to a first temperature ($T=T_1$) above or at the freezing point of water, but below or at the equilibribrium temperature ($T=T_0$) for generation/dissociation of hydrate; and also adapted to control the pressure within the generating zone (1),

and in

2) a cooling zone (80) which is associated with

- means (16,93,88,87,86,96) adapted for supplying and possibly recirculating and cooling of a second cooling medium which is to be supplied to the cooling zone (80) at a second temperature ($T=T_2$) being below the freezing point of water, and
- means (90,91,51) adapted for pressure releasing and delivering of an end product comprising particles of substatially ice free hydrate suspended in a liquious, but water-free hydro-carbon medium including residual amounts of the first and/or the second cooling medium.

18. A plant according to claim 17, c h a r a c t e r i z e d in that it further includes means (8,9) adapted for transferring an intermediate product including a hydrocarbon-saturated and substantially water-

and ice-free hydrate suspended in the first cooling medium, from the hydrate-generating zone (1) to the cooling zone (80).

19. A plant according to claim 17 or 18, c h a r a c t e r i z e d in that the hydrate-generating zone (1) and the cooling zone (80) substantially consist of two separate pressure-resistant tanks or containers (2,81).

20. A plant according to one of the claims 17-19, c h a r a c t e r i z e d in that the hydrate-generating zone (1) and the cooling zone (80) comprise one single pressure resistant tank or container (2') which in alternating periods is adapted to act as a hydrate-generating zone (1) and a cooling zone (80) respectively.

21. A plant according to one of the claims 17-20, c h a r a c t e r i z e d in that the hydrate-generating zone (1) comprises two or several parallel hydrate-generating zones, each including their own pressure resistant container and each adapted to operate simultaneously but in separate and time-shifted process cycles.

22. A plant according to claim 17 or 18, c h a r a c t e r i z e d in that each hydrate-generating zone (1) and cooling zone (80) comprises one single pressure-resistant container or tank (2'), where the upper part of said container or tank is adapted to act as a hydrate-generating zone (1) while its lower part is adapted to act as a cooling zone (80).

23. A plant according to one of the claims 17-22, c h a r a c t e r i z e d in that each cooling zone (80) is connected to a sluice (60) adapted to transfer the end product to a storage/user/transport-zone (50) having a pressure below the working pressure in the cooling zone (80).

24. A plant according to one of the claims 18-23, c h a r a c t e r i z e d in that said means (8,9,35,36) for transferring the first intermediate product from the hydrate-generating zone (1) to the cooling zone (80) comprises a narrow passage (35,36), adapted to limit the transport of the first cooling medium from the hydrate-generating zone (1).

25. A plant according to one of the claims 17-24, c h a r a c t e r i z e d in that it comprises means (31,32;97,98;55,56) adapted for mixing and stirring the components in the liquid phase in the hydrate-generating zone (1), in the cooling zone (80), and/or in the storing zone (50).

26. A plant according to one of the claims 17-25, c h a r a c t e r i z e d in that the means (87,88) for cooling of the second cooling medium, is adapted to provide a cold, second cooling medium in such an amount and at such a temperature ($T=T_2$) that the hydrate will be cooled down to a temperature ($T=T_0$) at which the hydrate is stable at the ambient air pressure.

27. A plant according to one of the claims 17-26, c h a r a c t e r i z e d in that the means for supplying water and the means for supplying the hydrate-forming hydrocarbon, respectively, comprise separate, atomizing nozzles (6,17).

28. A plant according to one of the claims 17-27, c h a r a c t e r i z e d in that it comprises

- means adapted for separation of a portion of the first cooling agent from the first intermediate product and/or a portion of the first and the second cooling medium from the end product,
- means adapted for cooling down the separated amounts of cooling agent, and

- means adapted for recirculating the first and/or the second cooling agent, direct cooling of the respective product.

29. A product saturated with hydrocarbon in the form of a hydrate from at least one hydrate-forming hydrocarbon suspended in a hydrocarbon liquid,
c h a r a c t e r i z e d in that the product is a suspension of a solid, hydrate-containing material in a liquid hydrocarbon carrier medium at a storage temperature ($T=T_4$) below the freezing point of water, whereby the liquid hydrocarbon carrier medium has an vapour pressure which at storage temperature is below a storage pressure corresponding to the ambient atmospheric pressure, which product can be manufactured according to a method as stated in claim 1.

30. A product according to claim 29,
c h a r a c t e r i z e d in that the storage temperature is so low that the hydrate is maintained stable at a storage pressure substantially equal to the surrounding pressure.

31. A product according to claim 29 or 30,
c h a r a c t e r i z e d in that the total volume of the solid hydrate-containing material is substantially higher than the total volume of the hydrocarbon carrier medium, preferably equal to or above 70 volume-% of the total volume.

32. A product according to one of the claims 29-31,
c h a r a c t e r i z e d in that the storage temperature is below -7°C, and preferably between -10°C and -35°C, and that the hydrocarbon carrier medium has an vapour pressure which at the storage temperature is below or approximately equals 1 bar.

33. A product according to one of the claims 29-32, characterized in that the solid, hydrate-containing material in the product has a gas content corresponding to a density of at least 130 $Sm^3/m^3$, preferably above 150 $Sm^3$ gas/$m^3$ solids.

34. A product according to one of the claims 29-33, characterized in that the hydrocarbon carrier mainly comprises hydrocarbons having at least 5 carbon atoms in the molecule, preferably a $C_5$- to $C_{10}$-petroleum fraction, and in particular a condensate fraction.

35. A product according to one of the claims 29-34, characterized in that the solid, hydrate-containing material in the product is made up of finely distributed hydrate particles.

36. A method according to one of the claims 1-16, characterized in that the process conditions in step a) are set in such a manner that an end product is obtained in which the solid, hydrate-containing material has a gas content corresponding to a storage density of at least 130 $Sm^3/m^3$, and preferably above 150 $Sm^3/m^3$ solids, when methane is used as the hydrate-forming hydrocarbon.

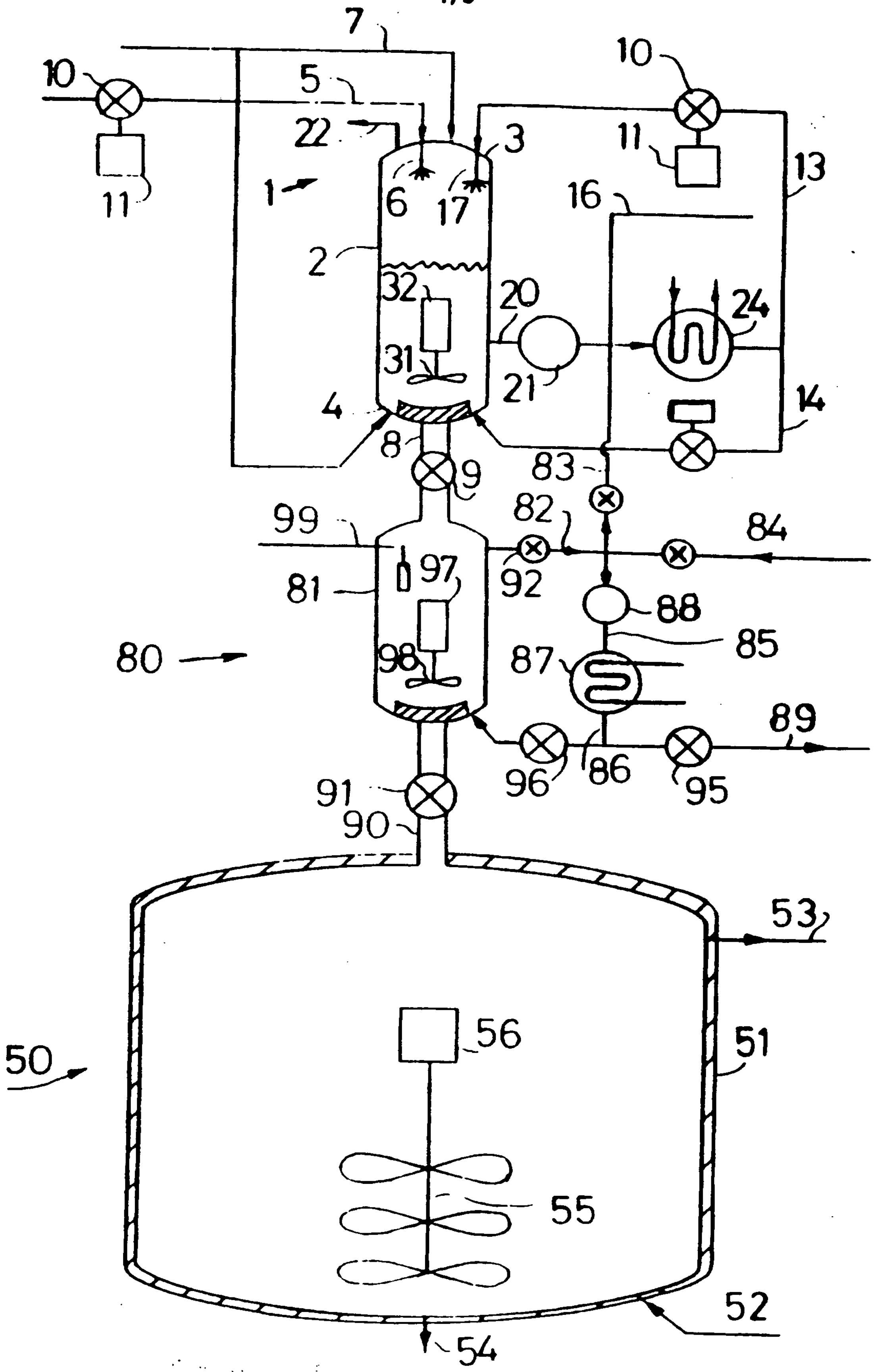
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Fig. 1

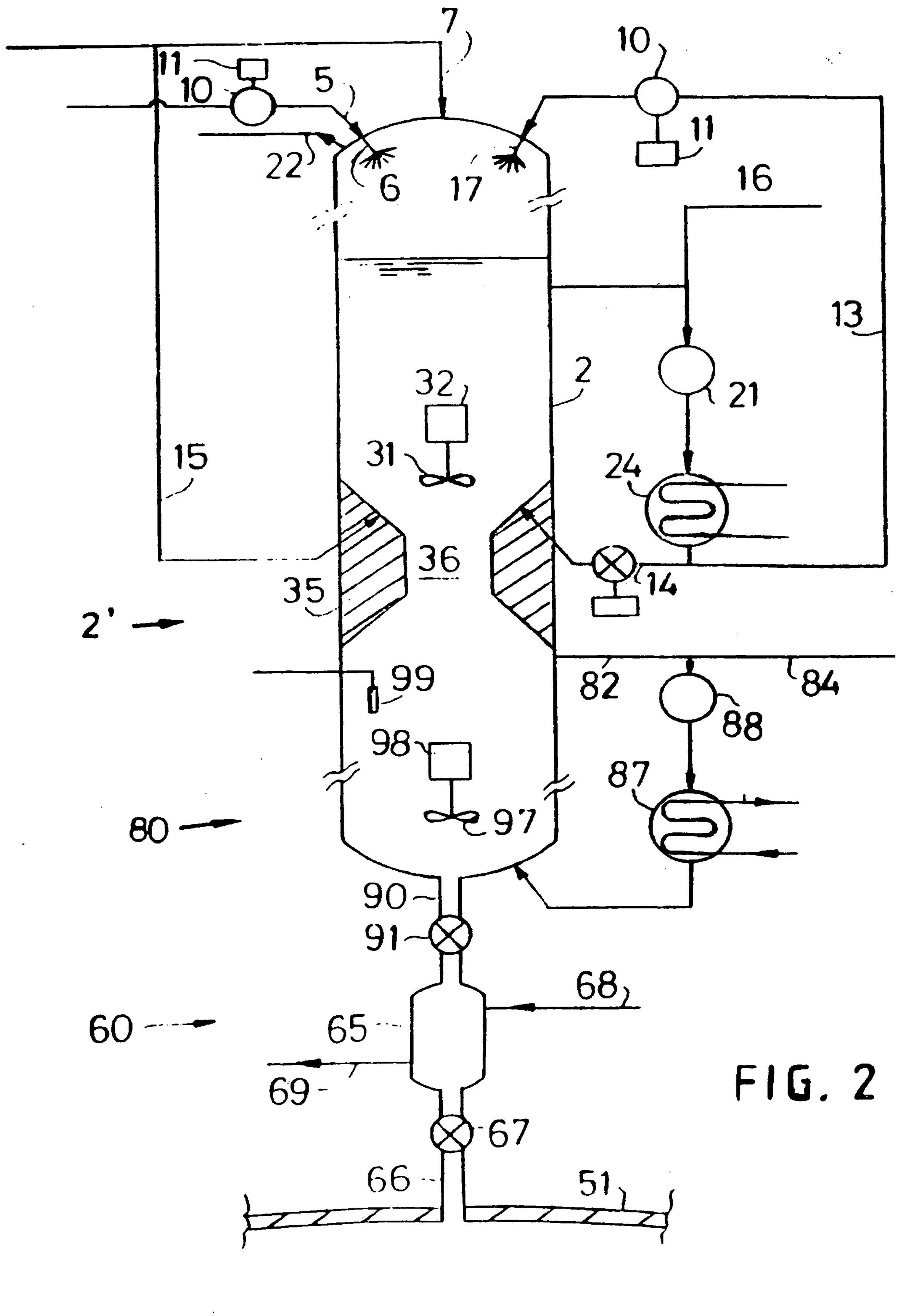
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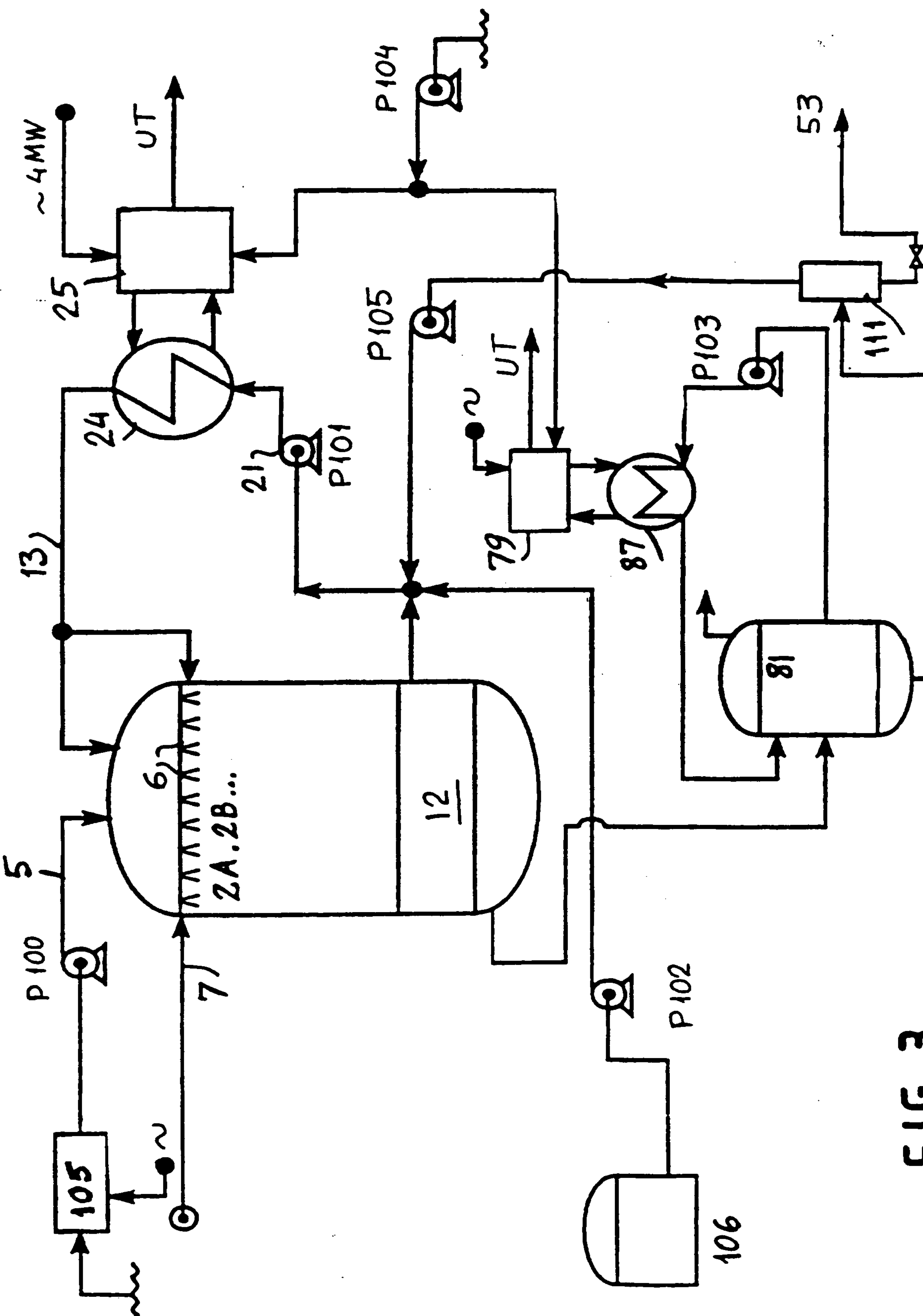
FIG. 2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2A.2B...
5
P100
105
~
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P102
106

FIG. 3

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 96/00099

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC6: F17C 11/00, F25J 1/02
According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC6: F17C, F25J, B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, CLAIMS

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | WO 9301153 A1 (GUDMUNDSSON, J.S.), 21 January 1993 (21.01.93) -- | 1-36 |
| A | WO 9400713 A1 (DEN NORSKE STATS OLJESELSKAP A.S.), 6 January 1994 (06.01.94) -- | 1-36 |
| A | US 2356407 A (A.J.L. HUTCHINSON), 22 August 1944 (22.08.44) -- | 1-36 |
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[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
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| Date of the actual completion of the international search | Date of mailing of the international search report |
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| 23 Sept 1996 | 24 -09- 1996 |

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# INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 96/00099

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | US 3514274 A (R.P. CAHN ET AL), 26 May 1970 (26.05.70) | 1-36 |

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

05/09/96

International application No.
PCT/NO 96/00099

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
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| | | EP-A- 0594616 | 04/05/94 |
| | | NO-A- 900395 | 30/07/91 |
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| | | NO-A- 922575 | 30/12/93 |
| US-A- 2356407 | 22/08/44 | NONE | |
| US-A- 2363529 | 28/11/44 | NONE | |
| US-A- 3514274 | 26/05/70 | NONE | |

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the relative amounts of materials will be made to secure an energy balance during the generating process.

To determine the required supply of cooling medium relative to the supply of hydrate-forming water, the heat-energy balance will now be considered. Generally, the heat balance over the reactor may be stated as in the following expression (enthalpi changes because of a possible pressure change in the gas is not taken into account)

$$q_{water}+q_{gas}+q_{medium}+q_{hydrate}+q_{system} = 0 \qquad (1)$$

where q represents the heat transport expressed as heat energy per unit of time, and the indexes refer to each single compound, i.e. $q_{medium}$ represents the effect from the cooling medium in the heating balance, $q_{system}$ refers to the heat transport between the reactor and the surroundings, etc. Below these references will be abbreviated to $q_v$, $q_g$, etc.

Each single term included in the heat balance (1) may be stated as a function of bulk transport, specific heat capacity and temperature differences, possibly also as enthalpi changes (for the hydrate generation) and the coefficient of thermal conductivity (for the heat transport) between the reactor tank and its environment. If, as a first approximation, it is assumed that the values of the heat capacity and the thermal conductivity are constant with respect to temperature changes, the heat balance (1) may be written as follows:

$$m_vC_v(T_v-T_d)+m_gC_g(T_g-T_d)+m_mC_m(T_m-T_d)+\Delta H_hm_h+m_hC_h(T_h-T_d)+q_s=0 \qquad (2)$$

The symbols in equation (2) has the following definitions:

$m_v, m_g$ etc. = bulk transport for each single component, positive values (represent transport) into the system and negative values out from the system.

| | | |
|---|---|---|
| $C_v$, $C_g$ and $C_m$ | = | specific heat capacity of water, gas and cooling medium, respectively. |
| $T_v$, $T_g$ and $T_m$ | = | temperatures of water, gas and cooling medium supply, respectively. |
| $T_d$ | = | average working temperature in the hydrate-generating reactor, more specifically the final temperature in the mixture of hydrate and cooling medium in the lower portion of the reactor. |
| $T_h$ | = | equilibrium temperature for generating or/dissociation of hydrate. |
| $\Delta h_h$ | = | generation-enthalpi for hydrate. |

The working temperature, $T_d$, will be somewhere between the freezing point of water (appr. 0°C) and the theoretical hydrat generating temperature, $T_h$. In many circumstances the temperature $T_d$ will, when generation of hydrate according to the present invention is of interest, be very close to the temperature in the surroundings $T_o$. The heat transport $q_s$ towards the environment will accordingly have a small value when compared to some of the other components contributing to the heat balance as expressed in equation (2).

The heat energy balance over the hydrate generator as found by equation (1) or (2), states the relations between the different variables (bulk transport and temperature of the different components). From equation (2) e.g. the following conditions for manufacturing of hydrate without free water may be found:

$$m_m \geq -\frac{m_v C_v (T_v - T_d) + m_g C_g (T_g - T_d) + \Delta H m_h + m_h C_h (T_h - T_d) + q_s}{C_m (T_m - T_d)} \qquad (3)$$

As according to this invention it is presumed that all water shall be converted into hydrate, the following equation must be satisfied

$$m_h = m_v + m_g \qquad (4)$$

The relation between gas and water in the hydrate will be defined by the socalled stuffing or packing density $\alpha$ which refers to the number of unit volumes of gas (expressed in standard cubic meter)($Sm^3$) that are incorporated in 1 cubic meter hydrate. This stuffing density $\alpha$ in general will be between 150 and 180. For natural gas the specific weight is approximately 0,735 $kg/Sm^3$ (at 15°C and 1 atmosphere) meaning that hydrate in dry condition will comprise between 110 ($\alpha$=150) and 132 ($\alpha$=180) kg for each cubic meter of hydrate. The exact amount of gas (expressed in weight units) being bound in each cubic meter of dry hydrate, should in practice be established from measurements of the stuffing density $\alpha$ obtained. The relations between the volume flow of hydrate, water and gas, determined by equation (4), therefore will be determined with a desired accuracy when one of the flows, for example the supplied amount of water, is known.

The heat exchange with the surroundings, $q_s$, will depend on several parameters such as the size of the plant, the design and materials used, and accordingly has to be calculated or determined by experiments in each single case.

In many uses of the method according to this invention, the temperature difference between the surroundings and the inner portion of said hydrate-generating reactor will be rather small and accordingly the heat transport out from or into the reactor, $q_s$, will be small related to other contributions to the heat balance, so that this contribution may be omitted in a first approximation.

The working temperature, $T_d$, generally will be slightly below the equilibrium temperature, $T_h$, for hydrate generation/desintegration, e.g. 3 or 4°C below $T_h$ at a pressure of 60 bar. Stronger cooling during the hydrate generation of course will lead to a lower working temperature. During the hydrate generation itself the working temperature should not be lowered substantially below 0°C to avoid generation of ice instead of hydrate at this step in the process. The equilibrium temperature for hydrate generation/desintegration may

be found in the literature or estimated from calculations.

Information related to the enthalpi during generation of gas hydrate from different hydrate-forming gases, may also be found in literature, calculated, or determined by experiments. For some uses it is sufficient to estimate the enthalpi for the generation process to approximately 95 kcal/kg.

The remaining terms in the expression (3) are either constants ($C_v$ etc.), temperature values ($T_v$ etc.) given from existing conditions or selectable values. A sufficient exact value of the minimum supply of cooling medium may be found from the equation (3).

The most important components in equation (3) will in many cases be $\Delta hm_h$ and $C_m(T_m-T_d)$. However, if $T_v$ and $T_g$ are below the value of $T_d$, there is reason to believe that the contribution from water and gas supply will be balanced by the contribution from the cooling of generated gas hydrate, $m_hC_h(T_h-T_d)$.

When the above premises are met the reaction described in equation (3) may be simplified to

$$m_m \geq \frac{\Delta H m_h}{C_m(T_d-T_m)} \qquad (5)$$

The expression (5) may be used in these examples to estimate the relation between the supply of water and the supply of cooling medium calculated from the specific heat capacity of the cooling medium, $C_m$, the temperature difference between the cooling medium at the input and at the output, $T_d - T_m$, the balance between the masses (4) and the composition of the bulk gas hydrate mass as stated by the stuffing density $\alpha$. Values of the hydrate generation heat, $\Delta H$, may be found in the literature.

The following example illustrates the use of expression (5) for calculating the required supply of a cooling medium.

A condensed fraction having a specific heat capacity of

1.58 kJ/°K kg is used as a cooling medium. The cooling medium is supplied to the hydrate-generating zone having a temperature of -35°C. The working temperature $T_d$ in the hydrate-generating zone will be approximately 10°C at a pressure of 60 bar. Calculated or obtained stuffing density is 175, which leads to a gas hydrate compound containing 175 x 0,735 = 129 kg gas/$m^3$.

The generation enthalpi for hydrate, as mentioned above, is approximately 95 kcal/kg or approximately 398 kJ/kg. Inserted for ΔH in equation (5) this gives:

$$m_m \geq \frac{398 \cdot 940}{1,58(10-(-35))} = 5.262\ kg/hour$$

when generation of 1 $m^3$ (=940 kg) gas hydrate is considered. The gas hydrate mass will contain 940-129 = 811 kg of water. The condensate at a temperature -35°C therefore has to be supplied at a rate exceeding 5262/811≈6,5 related to the amount of water, to ensure that dry hydrate is produced.

It has not been previously known how important it is that the hydrate should not include free water. Just this recognition may be taken as the basic feature of the present invention. The present invention as defined in the claims below comprises a method of producing "dry" hydrate, a method of producing a suitably composed hydrocarbon product from the dry hydrate, a plant adapted for implementing said methods and the product itself; and the invention implies all the advantages and meet all the requirements stated in the specification.

According to a preferred method the first cooling medium does not include free water and may preferably consist of liquid hydrocarbon or a liquid hydrocarbon composition, and this first cooling medium is used for direct cooling down to a temperature preferably just above 0°C during the generating process; whereupon a second cooling medium, also without any free water, is used for further cooling of the product down to a temperature well below 0 C.

The first and the second cooling mediums may be represented by the same liquid or by two different liquids.

To give a still better understanding of the present invention reference is made to the more detailed description of an embodiment of a preferred plant for manufacturing dry gas hydrate, that is hydrate without any free, converted water, and a further description of the product itself. While the function of said plant is described, this will at the same time give a description of the method according to the invention. In this connection reference is also made to the drawings in which:

Figure 1 illustrates a simple basic embodiment of the plant according to the present invention,

Figure 2 illustrates a somewhat different embodiment of the plant according to the present invention, where the hydrate-generating zone is separated in two chambers within a common container, and

Figure 3 illustrates in some more detail an implementation of a plant including some specifications in particular of the relative volumes of the throughput.

It is to be noted that the same reference numbers are used in all figures when practical. It should also be noted that the figures do not illustrate all details in the plant, but emphasize the portions of the process which are essential to understanding the present invention, without overloading the drawings. Finally it should be mentioned that the different figures and parts of same are not necessarily shown at the same scale.

Here follows a short description of the main components included in the plant as shown i Figure 1.

The plant comprises a reactor 2 with a supply pipe 5 for water and two further supply pipes 7 and 15 for one or more hydrate-forming hydrocarbons. Generally these hydrocarbons, at least partly, are supplied as a gaseous medium. All the supply lines are preferably provided with the necessary valves such as 10 and control or regulating

devices for these valves, such as 11. In close connection to the reactor 2 there is an external temperature control system including a heat exchanger 24 connected to a source 25 of cooling medium, at least one supply channel 13, 14 for said cooling medium, preferably a liquid, an outlet 20 for a cooling medium from the reactor 2, and the required pumps such as 21, valves such as 18, and control or regulating devices for these, such as 19 and similar conventional components. The parts of the plant which so far have been mentioned, make up the hydrate-generating zone 1.

Below the hydrate-generating zone 1 there is arranged a cooling zone 80 which in one hand comprises a cooling container 81 with an inlet 8 for an intermediate product produced in the reactor 2, provided with an inlet valve 9. Still further down the cooling container 81 is provided with an outlet 90 for the finished hydrocarbon product or the end product. This outlet 90 is equipped with a suitable outlet valve 91.

In connection with the cooling container 81 there is provided a further temperature controlling, external circulation loop comprising a heat exchanger 87 which is connected to a cooling medium source 79 (which may be identical to the above mentioned coooling medium source 25), and which is connected to the cooling container 81 via the outlet 82, the inlet 86, and the required pumps 88 and valves 92, 93, 94, 95, 96. The cooling medium used may be supplied from the inlet lines 16 and/or 84.

The plant still further comprises a storage tank 51 which in its upper part is provided with an inlet 90 and in its lowermost part an outlet 54. The storage tank 51 may preferably be provided with a stirring device 55 driven by a motor 56 and may in addition be connected to an external temperature control system being only indicated in the figure by means of the outlet 53 and the inlet 52; as it is implied that the substance removed from the storage tank 51 via the outlet 53 may be circulated through a heat exchanger (not shown in the figure) returning to the storage tank 51

via the inlet 52 when the required temperature has been obtained, similar to the cooling loops shown in connection with hydrate-generating zone 1 and cooling zone 80.

For an overview the process will be divided below in two steps:

STEP a: THE GENERATING OF HYDRATE

In the plant according to Figure 1 water is led together with gas or another hydrate-forming and hydrocarbon-containing fluid, to the reactor 2 at such pressure and temperature conditions that hydrate 12 is formed, but as already mentioned, in such a manner that there will be no excess water in the tank. This may e.g. be ensured by using a control loop, whereby a detector (not shown) at the bottom of the tank 2 dilivers a control signal back to the control units 11 as soon as traces of water are detected, and the control units 11 then in turn control the setting of the valves 10. As another example there may exist predetermined limits for setting of the different valves in such a manner that water never will gather at the bottom of the tank. A first, cold, liquid cooling medium, which does not include any water, e.g. a condensate of natural gases, is supplied to the reactor 2 in a controlled amount and at a controlled temperature via the loops 16, 24, 13, 14 so that the temperature in the reactor 2 is maintained within the hydrate-forming limits related to the prevailing pressure in the reactor. The relation between the amount of water supplied at 5, the amount of cooled first cooling medium and gas as supplied at 7, is regulated or controlled as already suggested, in such a manner that all the water supplied to the reactor 2 is converted into hydrate. The first cooling medium which is heated due to the generation of hydrate, or at least a certain part of said medium, if required may be separated, e.g. by filtering, from the generated hydrate (or it may be treated together with said hydrate); is taken out of the reactor 2 at 20 and

then cooled in the external heat exchanger 24, whereupon this first cooling medium is recirculated via the connections 13 and 14 and transported back to the reactor tank 2 to cause further cooling of the contents of the reactor tank, preferably by direct contact with the product within the tank. The hydrate 12 already at this stage of the process will consist of a particulate mixture or suspension of "dry" hydrate, i.e. hydrate without any free water, and the above mentioned first cooling medium which does not comprise water. The temperature of this mixture or this intermediate product, is somewhere between the temperature of the first cooling medium and the temperature limit or equilibrium level for hydrate generation at the prevailing pressure in the reactor tank 2. Normally the prevailing pressure during the hydrate generation will be rather high, e.g. 60 bar. And all the tanks, pipes and control components (in the generating zone) of course have to be dimensioned to endure such a high pressure.

STEP b: COOLING OF HYDRATE

When the intermediate product has been transferred to the cooling tank 80 via the connection 8 and the controllable valve 9, further cooling takes place by means of an external cooling loop 82, 88, 85, 86, 86, 96 for a second cooling medium. The first cooling medium included in the intermediate product which is generated in step a, is removed totally or partly and replaced by this still colder second cooling medium. This second, colder cooling medium preferably has such a temperature and is provided in such an amount that the hydrate is maintained stable down to one atmosphere pressure, or approximat ly 1 bar a. Then a second intermediate product is obtained and this comprises dry hydrate as particles and a cooled, water-free cooling medium (possibly including a mixture of the first and the second cooling medium); and this second intermediate

product is transferred via the connection 90 and the valve 91 to the storage tank 51 and is stored as cooled down, preferably at one atmospheres pressure. The volume relation between the cooling medium and the hydrate particles is maintained low, however, not so low that not a certain portion of the cooling medium may be separated from this second intermediate product for circulation and cooling. This is illustrated in Figure 1 as the storage tank 51 receives the second intermediate product via the connection 90 and the valve 91, while portions of the other cooling medium may be circulated and are temperature controlled via the outlet 53, the inlet 52 and a heat exchanger (not shown on the figure). The second cooling medium may possibly have a similar or an identical composition as the first cooling medium, such that the only difference is the working temperature. However, the two cooling media may also have different compositions. It is mentioned in particular that one or both media may comprise selected hydrate-forming components.

The process described briefly above will be explained more in detail below and then based on two different embodiments shown in Figure 1 and Figure 2, respectively.

In a basic production plant all components shown in Figure 1 may be used, such as reactor 2, cooling tank 80 and storage tank 51.

A hydrate-forming hydrocarbon (preferably substantially in gasform) is supplied to the reactor 2 through the pipe 7, while water is supplied via the pipe 5. The amount of water supplied is controlled and limited dependent on other parameters such as pressure and temperature; so that preferably all supplied water is converted into hydrate in the reactor 2. In this connection the equilibrium conditions in equations 3 and 4 above are referred to. The hydrate is formed, if the water enters and is atomized through the nozzles 6, as small, crystaline particles falling down in the tank 2, like snow flakes. Heat energy liberated during

the hydrate generation is removed by direct flushing with the first cooling medium, preferably condensate, which in a cooled condition is supplied through a line 13 and preferably also through a nozzle 17 in the reactor tank 2, and possibly also through a pipe 14 entering close to the bottom of the reactor tank 2. It should be mentioned that gas and water may be brought together in a different way, e.g. small bubbles of gas may be led through a bath of water. The essential matter is that water and gas are in direct contact with each other, and has a large common surface while a long reaction time is allowed. In both these examples the height of the tank 2 is important. The higher the tank the longer is the reaction time which may be obtained.

The heated cooling medium is drained or drawn out of the reactor tank 2 through a pipe 20, and is cooled in a heat exchanger 24 before returning to the reactor tank 2 via the tubes 13 and/or 14. The first cooling medium which is supplied to the reactor tank 2 may, if desired, include a fraction of light hydrocarbons which together with the supplied gas may be converted into hydrate when brought into contact with water.

Thus a suspension or slurry is generated comprising hydrate and also a liquid first cooling medium at the bottom of the reactor tank 2. This mixture will have a relatively high temperature, e.g. 10-15°C, but will not include any free non-converted water. To ensure that this mixture, which may be referred to as a first, intermediate product, does not include any free water, the supplied amount of water is controlled and/or limited as explained above, and possibly the supplied first cooling medium in addition incorporates some hydrate-forming components which will imply that occurring small amounts of free water also will be converted into hydrate.

When the desired amount of this intermediate product has been generated in the reactor container 2, a volume of the intermediate product is conveyed via the pipe 8 and the valve 9 out to a cooling tank 81 in the cooling zone 80. The

content of the heated, first cooling medium in this intermediate product is completely or partly substituted by a second, heavily cooled cooling medium, and this cold, second cooling medium is supplied to the cooling tank 81, (e.g. at a temperature of -10 til -20°C or possibly still lower), through a pipe 86 and a valve 96. Remaining portions of the relatively hot first cooling medium 102, will be expelled and replaced by the second, cold cooling medium and is then returned to the reactor circuit 1 via tubes and valves 92, 82, 93 and 83.

When the intermediate product has been cooled down in the cooling zone 80, it is applied via a tube 90 and a valve 91 to a storage tank 51 in which the product (which now is referred to as the end product as soon as a stable final temperature has been obtained) preferably is stored at a temperature which gives an end product being stable at atmospheric pressure and at a specified temperature e.g. -10°C or lower, possibly down to -40°C.

To avoid strong pressure pulses in the process plant, the pipes leading to and from the cooling tank 81, being the first place where a low pressure exists, are equipped with valves 92, 96 which may be closed when the valve 91 is opened.

A somewhat different embodiment of the present invention is shown in Figure 2. The method used is, however, substantially the same as already explained, but the plant itself may have a simpler design. In the plant according to Figure 2 both the generation and the cooling of the hydrate suspension is undertaken in one common tank 2'. A restriction 35 will, together with a sufficient supply of a cold second cooling medium, ensure that the lower portion (the cooling zone 80) of the reactor tank 2', all the time is filled up by a cold, second intermediate product. A sluice assembly 60, allows transmission of the hydrate compound from the high pressure zone 1 (uppermost in the reactor tank 2') to the low pressure zone in the storage tank 51 without generation and transmission of high pressure pulses within

the plant. It should be noted that the second, cold cooling medium may be supplied to the sluice assembly 65 through the pipeline 68 from a low pressure reservoir, is led out from the sluice volume 65 through the pipeline 69 and e.g. into the cooling circuit for the lower portion, i.e. the cooling zone 80 of the tank 2', via the pipeline 84.

The reactor 2' and the containers 81 and 51 can preferably be equipped with thermally insulated walls in a manner known per se.

The reactor 2' may preferably also be equipped with water detectors close to the bottom level, for detection of collected water, or may possibly be provided with a view glass for visual observation of precipitated water. Such detectors may be adapted to transmit signals for the control of valves for supplying water and/or cooled hydrocarbon medium, so that the conditions for production of water-free hydrate are maintained or re-established. An operator may possibly correct the flow rates according to the indications of water at the bottom of the reactor 2'.

Inert components, i.e. gaseous components which cannot be converted into hydrate at prevailing process conditions, as e.g. nitrogen, oxygen, rare gases, hydrogen etc., ought to be removed from the reactor 2 or 2'. As an example a minor gas flow may be led from the top 3 of the reactor 2 through an outlet 22, preferably placed close to the top of the reactor 2 or 2'.

The pipes 5, used for the supply of water and the pipes 13, 14 used for cooling medium or condensate, ought to be provided with flow control means, e.g. controllable valves 10 or pumpes having adjustable flow rates, both provided with associated control units 11, so that these flows may be controlled to obtain suitable volume relations between the water and hydrocarbon supply, preferably as stated according the above stated heating balance.

The cooling tank 81 may preferably be equipped with a thermometer or another type of temperature detector 99, generating a signal representative of the temperature in the

suspension or the mixture of hydrate and hydrocarbons in the tank, and probably also pressure detectors (not shown) for sensing the pressure, so that the signals obtained may control the filling/cooling and/or emptying of the cooling container 81 and possibly also other process steps. It may be broadly suggested that the temperature in the hydrate-generating zone 1 is approximately 2-4°C below the equilibrium temperature for generating hydrate at the prevailing pressure, which here is relatively high, e.g. 10-40 bars. The temperature in the cooling zone 80 may be -10°C or still lower, and the pressure at the same place e.g. 1 bar. In the storage tank the temperature may be still lower, e.g. down to approximately -35°C and the pressure may then be equal to the ambient pressure.

In the specification above only the basic or quite necessary components are mentioned and the relative volumes are not exactly stated.

A more precise and full description of a complete plant for cooling of hydrate by means of recirculated condensate follows below with reference to Figure 3. In connection with the description below there are included some specific values in the form of calculated examples, which only should be considered as approximate values without any limiting effects on the implementation of this invention.

In the hydrating process shown, fresh-water is used as a hydrate basis, and recirculated condensate is used as a cooling medium. Both the hydrate generation and the output of the finished product takes place continuously.

The fresh-water used may be generated by desalting of sea water in a fresh-water generator 105. The fresh-water generator 105 may itself consist of one or more sea water pumps (P100) and batteries of semipermeable diaphragms, through which the desalting takes place. The sea water is pumped until a pressure of 60 bars has been reached, before feeding it towards the diaphragms. The fresh-water leaves the system at 15 bar a.

The hydrate water is fed together with cooled and

recirculated condensate at 0°C to a plurality of containers 2 assumed to be connected in parallel (only one is shown), and these feeding flows are distributed evenly over the total volume and are contacted with the natural gas feed supplied via the pipe 7, via nozzles 6 installed in the ceiling and at the cylinder walls. The hydrate generation takes place at 60 bar a, and a suspension or slurry comprising hydrate and condensate, builds up on the bottom of the reactor 2 where the temperature is approximately 15°C, which here is the equilibrium temperature. The amount of natural gas supplied to the reactors via the input 7 is estimated to 700.000 $m^3$/day.

The condensate which takes up the heat energy dissipated during the hydrating process, is discharged from the reactors 2, cooled down from +13° - 0°C in the recirculating cooler 24 which e.g. may be connected to a propane cooling circuit 25 and then recirculated to the reactors 2. The amount of hydrating heat which has to be removed, will be approximately 21 MW. The recirculating loop is equipped with a recirculating pump 21 for condensate.

The hydrate suspension 100 representing an intermediate product, is removed from the bottom of the reactor(s) 2 and sent to a cooling container 81 where the hydrate suspension 100 is cooled down to -20°C. This cooling is provided by a cold condensate circuit 87, connected to the cooling container 81, in which filtered condensate is delivered from the cooling container at -20°C and cooled down to -30°C in the condensate circulation cooler 87, and returned to the cooling container 81. In the cooler 87 the cooling takes place by evaporation of propane at -40°C. The flow of propane is supplied to a propane cooling circuit 79 which comprises a cooling circuit compressor and a propane condensate which may be based on sea water. This cooling circuit 79 may possibly produce frost, in the shape of refridgerated propane, both to the recirculating cooler 24 and the condensate cooler 87.

The cooled suspension from the cooling container 81 is

supplied to a hydrate/condensate separator 111, from which the end product is taken out as a hydrate paste consisting of approximately 20 volume-% condensate and approximately 80 volum-% hydrate, to be stored at atmospheric pressure. The separated condensate is (at 111) mixed with the added condensate from a condensate store 106 and with recirculated condensate in the cooling loop 2, 24 for the reactor, and this mixture is supplied to the recirculating cooler 24.

In addition the plant shown in this figure comprises the following components treating the below mentioned chemicals at the conditions listed:

| | |
|---|---|
| sea water taken in (at 5) | 913 $m^3$/hour |
| gas supply (at 7) | 700.000 $Sm^3$/day |
| hydrate generator (2A) | 60 bar, 13°C |
| output of sea water (from 2A) | 1098 $m^3$/hour |
| slurry valve (from 2A) | 673 $m^3$/hour, 0°C, 15 bar |
| cooling container (81) | 15 bar |
| circulating pump (for 87) | 274 kW |
| condensate cooler (87) | 5350 kW, -20°C to -30°C |

The first intermediate product consists of hydrate particles without any free, non-converted water, suspended in a first cooling medium/carrier liquid which e.g. may consist of a condensate having traces of hydrate-forming hydrocarbons. The amount of hydrate may here e.g. be 50% of the total volume of the intermediate product. The intermediate product therefore will have a low viscosity. The end product similarly comprises hydrate particles. These particles still are suspended in a carrier liquid or in a second cooling medium. It should be noted that a second hydrocarbon medium does not include substantial amounts of hydrate-forming hydrocarbons or compositions which easily may be liberated as wax or other liquid or solid components, and of course not any free water. Finally it should be mentioned that the amount of the hydrocarbon medium relative to the amount of hydrate preferably is less in the end product than in the intermediate product, e.g. approximately 20 volume-%, so that the end product more or less has the

consistenc of a paste. However, the application is not limited to just these volume relations, however, a preferred volume relation may be 70 volume-% hydrate and 30 volume-% solid matter.

During use and storage the hydrocarbon product may be relatively solid, acting as a rather compact paste, and may in addition be further compacted to obtain an increased energy content for each volume unit.

During transport the product may possibly be diluted by adding more of the second cooling medium, and may then be still simpler to handle with pumps etc.

Moreover, the plant may be constructed in many different manners. It may e.g. include only one reactor which can work batchwise, even if larger plants are preferred, including two or more reactors 2, connected in parallel and always working in different stages of the process. For a plant with several reactor tanks running in parallel, one common or several separate parallel cooling tanks 81 may be used, even if the most natural solution is to let all the generators discharge to a common storage tank 51. The composition of the different cooling media may also be the same so that the only feature distinguishing these media from each other is the temperature. However, it is preferred that only the first cooling medium comprises hydrate-forming components while the second cooling medium preferably is completely free of hydrate-forming components. All the cooling circuits described may also be replaced by corresponding conventional cooling circuits of other types.

The method, the plant and the product according to the present invention may be used in different industrial processes. Thus the invention may be used for converting a natural gas into a hydrocarbon product which may be stored and transported under conditions being simple to obtain from a technical point of view. The method may accordingly be used in connection with production and transporting of natural gas from primary gas fields, and in particular from remote gas fields to terminals arranged close to the user or

the market. Fluids from so-called associated gas fields, i.e. oil fields which in addition to the hydrocarbon liquid (oil) comprises greater or smaller amounts of gas components, may of course also be converted into hydrocarbon products of the kind mentioned above. The converting of such gas may then also represent a profitable oil and gas production, in particular from small and remote oil and gas fields.

Further this invention may be used where it is a need for taking care of and store volatile hydrocarbon components for a shorter or longer time period. Such needs may in particular exist at locations where an excess amount of gas is present in association with oil production locations and oil refining plants, in connection with loading, unloading and transporting of crude oil, for collecting volatile components (VOC) from the crude oil, for loading of refined products as petrol, diesel oil etc.

The product according to this invention may be used for different purposes, e.g. as a medium for storing and transporting natural gas, as fuel for energy producing machines or in heating plants, and as a source for natural gas components and light hydrocarbon liquid components which may be treated and refined in different manners in chemical plants. It may in particular be suitable to use the product as fuel for vessels e.g. as an environmental conserving fuel for ferries.

The plant according to the invention may be installed on vessels or platforms offshore or may be built as stationary plants on land.

In order to further explain what is shown in Figure 3, the following is remarked, whereby Figure 3 in the following text is described from the inlet to the plant at the upper left part of the figure, to the outlet from the plant at the lower righthand part of the figure.

The two inlets shown to freshwater generator 105 indicate that the freshwater generator in the first place has an inlet for seawater, which typically can be 913 $m^3/h$ or

0,254 $m^3/s$. These and other magnitudes in the following description however, are only meant to be examples of typical values. The other input to freshwater generator 105 indicates that it also needs a supply of electric power, and the power consumption is stipulated to be 2355 KW. The freshwater flowing out of freshwater generator 105 will then be present at a pressure of about 15 bar and in an amount estimated to be 138 $m^3/h$. This freshwater passes through a pump denoted P-100 which can increase the water pressure by 40 bar and this pump will then have a power consumption of 219 KW. The hydrate water being led into the reactor(s) 2A, 2B and so forth through supply pipe 5 typically has a temperature of 15°C. The pressure in the hydrate-generating reactor 2A, 2B is typically 60 bar, whereby the gas flowing in through supply pipe 7 and nozzles 6 are supplied to the oil and gas processing plant in an amount estimated to about 700,000 Sm·/day.

From supply pipe 13 condensate at about 0°C flows into the reactor(s) and this comes from the resirculation cooler 24 which may have a cooling requirement of about 21 MW and the cooling circuit 25 preferably can be a propane cooling circuit having a power consumption somewhat above 4 MW. The pump P-104 supplies cooling water from a seawater source in an amount of about 4,000 $m^3/h$ and with a power consumption of about 790 KW. The seawater leaves the propane cooling circuit 25 through outlet UT.

Some of the cooling water from the seawater inlet is passed from pump P-104 to another propane cooling circuit 79 which has a power consumption of about 2 MW. The amount of seawater flowing thereto can be about 1,000 $m^3/h$. It is to be noted however, that propane cooling circuits are referred to here only as an example of cooling circuits, since all conventional cooling circuits can be employed as long as the capacity is sufficient. This will also be seen from the application as a whole. The object is here that the circulation cooler 87 shall be able to deliver condensate at a temperature of about -30 C into the upper inlet to cooling

tank 81. The condensate being here used for cooling comes from a condensate/hydrate slurry being formed in generator 2 underneath the hydrate layer 12 and being introduced into cooling tank 81 through the lower inlet therein, at at temperature of about 15°C.

The plant also uses condensate from a condensate storage 106 in an amount of about 40 $m^3/h$, and this condensate is lead through pump 102 and pump 101, also denoted 21 i Figure 3, to the resirculation cooler 24. An intermediate product in the form of a slurry at a temperature of about -20°C and a pressure of about 60 bar is discharged at the bottom of cooling tank 81 and is conveyed to a hydrate/condensate separator 111 which in part direct condensate back into the system through pump P-105 and in part conveys the hydrate product, which can typically be in paste form, out through outlet 53 for storage and transport.

Moreover in Figure 3 there are included necessary pumps and valves in order that the plant shall be able to operate.

# C L A I M S

1. A method for manufacturing a hydrocarbon product comprising a hydrate of at least one hydrate-generating hydrocarbon, wherein

a) the hydrate-forming hydrocarbons and water are brought together in a hydrate-generating zone (1) at hydrate-generating pressure and temperature conditions,

c h a r a c t e r i z e d in that

the heat energy liberated during the generation of hydrate is removed by means of a first liquid and anhydrous cooling medium which is brought to flow through the hydrate-generating zone (1) in such quantities and at a first temperature ($T=T_1$) being so low that hydrate is generated, but not being so low that frozen water is generated in an irreversible manner in more than insignificant quantities; the relative quantities of the supplied water and the supplied first cooling medium being set so that substantially all water is converted into hydrate; thereby generating a first intermediate product comprising hydrate particles of a hydrocarbon saturated hydrate substantially free from water and ice and surrounded by or suspended in the first cooling medium, and that

b) an anhydrous and liquid second cooling medium is added to the first intermediate product in a cooling zone (80) at a second temperature ($T=T_2$) lower than the freezing temperature of water, to cool the first intermediate product further down to obtain an end product comprising particles of anhydrous, saturated gas hydrate surrounded by or suspended in the first and/or the second cooling medium, whereupon the end product is pressure released and removed from the cooling zone (80).

2. Method according to claim 1,

c h a r a c t r i z e d in that the partial pressure of the hydrate-forming hydrocarbons in the hydrate-generating zone (1) is above 15 bars, preferably above 30 bars; and

that the average temperature in the hydrate-generating zone (1) is maintained at a level which at a minimum is 2°C preferably approximately 4°C below the equilibrium temperature for generating/dissociating of hydrate at the present partial pressure of the hydrate-forming hydrocarbons, but above the freezing point of water.

3. A method according to claim 1 or 2, c h a r a c t e r i z e d in that the supplied amount of hydrate-forming hydrocarbons is maintained in excess related to the supplied amount of water in the hydrate-generating zone (1) during the complete generating process in the generating zone (1).

4. A method according to claim 1, 2 or 3, c h a r a c t e r i z e d in that the second cooling medium is supplied to the cooling zone (80) in such a quantity and at such a temperature ($T=T_2$) that the hydrate is cooled down to a temperature ($T=T_3$) at which the hydrate (12,101) is stable at a pressure corresponding to the surrounding air pressure.

5. A method according to one of the claims 1-4, c h a r a c t e r i z e d in that the steps a) and b) take place in separated pressure containers (2,81; Figure 1).

6. A method according to one of the claims 1-4, c h a r a c t e r i z e d in that the steps a) and b) are performed consecutively in one and the same pressure tank (2',81').

7. A method according to one of the claims 1-6, c h a r a c t e r i z e d in that the end product (103) after the completion of steps a) and b), is introduced into a pressure sluice (60) adapted for transport of the end product to a storage tank (51) having a pressure below the working pressure in the cooling zone (80), preferably

approximately 1 atmosphere.

8. A method according to claim 7, c h a r a c t e r i z e d in that the steps a) and b) are carried out in a unitary pressure container (2, Figure 2) which is divided in two parts and is provided with a narrow passage (35) between the hydrate-generating zone (1) and the cooling zone (80), restricting exchange/transport of cooling medium between the two zones.

9. A method according to one of the claims 1-8, c h a r a c t e r i z e d in that at least some portions of the second cooling medium is separated from the hydrate and sent to further cooling e.g. in an external heat exchanger (87) whereupon the cooled, second cooling medium is partly circulated back to the cooling zone (80), and is partly supplied to or allowed to flow into and mix with the first cooling medium in the hydrate-generating zone (1).

10. A method according to one of the claims 1-9, c h a r a c t e r i z e d in that the hydrate-generating hydrocarbons comprise hydrocarbon components included in natural gas and in particular in methane.

11. A method according to one of the claims 1-10, c h a r a c t e r i z e d in that the first cooling medium comprises hydrate-forming hydrocarbons.

12. A method according to one of the claims 1-11, c h a r a c t e r i z e d in that the cooling of the second intermediate product in step b) is carried out in the presence of hydrate-forming hydrocarbons until the temperature in the hydrate compound has reached a level lower than the freezing point of water, preferably a temperature at which the hydrate is stable.

13. A method according to one of the claims 1-12, characterized in that destabilizing amounts of volatile components present in the hydrate compound when it has been cooled down to a temperature at which the hydrate is substantially stable, is removed so that an end product is obtained in which the hydrocarbon carrier medium has a gas pressure which at the final temperature is below the final pressure.

14. A method according to one of the claims 1-13, characterized in that the portion of hydrocarbons not forming hydrate, in the first and/or in the second cooling medium, does not at all contain or contains only insignificant amounts of components which will settle as wax or another solid or high viscous material at the lowest temperature in the process.

15. A method according to claim 14, characterized in that the portion of non-hydrate-forming hydrocarbons in the first and/or the second cooling medium, substantially is made up of a $C_5$ to $C_{10}$-petroleum fraction, preferably a condensate fraction.

16. A method according to one of the claims 1-15, characterized in that water and/or the hydrate-forming hydrocarbons and the first cooling medium is supplied to the hydrate-generating zone (1) through separate atomizing nozzles (6,17).

17. A plant for manufacturing a hydrocarbon product, which plant comprises

- means (7) adapted for supplying hydrate-forming hydrocarbons,
- means (5,6) adapted for supplying water, and
- means (13,14,17) adapted for supplying and possibly recirculating a first cooling medium,

characterized in that the plant is divided

into

1) a hydrate-generating zone (1) which is connected to the above means, and

- means (10) adapted for controlling the relation between the amount of water supplied and the supplied amounts of the first cooling medium so that all or a substatial part of the water will be converted into hydrate (12) when hydrate-forming hydrocarbons and water are brought together in the hydrate-generating zone (1) at hydrate-generating conditions, and
- control means adapted to control a first temperature within the hydrate-generating zone (1) so that it corresponds to a first temperature ($T=T_1$) above or at the freezing point of water, but below or at the equilibrium temperature ($T=T_0$) for generation/dissociation of hydrate; and also adapted to control the pressure within the generating zone (1),

and in

2) a cooling zone (80) which is associated with

- means (16,93,88,87,86,96) adapted for supplying and possibly recirculating and cooling of a second cooling medium which is to be supplied to the cooling zone (80) at a second temperature ($T=T_2$) being below the freezing point of water, and
- means (90,91,51) adapted for pressure releasing and delivering of an end product comprising particles of substatially ice free hydrate suspended in a liquious, but water-free hydrocarbon medium including residual amounts of the first and/or the second cooling medium.

18. A plant according to claim 17, c h a r a c t e r i z e d in that it further includes means (8,9) adapted for transferring an intermediate product including a hydrocarbon-saturated and substantially water-

and ice-free hydrate suspended in the first cooling medium, from the hydrate-generating zone (1) to the cooling zone (80).

19. A plant according to claim 17 or 18, c h a r a c t e r i z e d in that the hydrate-generating zone (1) and the cooling zone (80) substantially consist of two separate pressure-resistant tanks or containers (2,81).

20. A plant according to one of the claims 17-19, c h a r a c t e r i z e d in that the hydrate-generating zone (1) and the cooling zone (80) comprise one single pressure resistant tank or container (2') which in alternating periods is adapted to act as a hydrate-generating zone (1) and a cooling zone (80) respectively.

21. A plant according to one of the claims 17-20, c h a r a c t e r i z e d in that the hydrate-generating zone (1) comprises two or several parallel hydrate-generating zones, each including their own pressure resistant container and each adapted to operate simultaneously but in separate and time-shifted process cycles.

22. A plant according to claim 17 or 18, c h a r a c t e r i z e d in that each hydrate-generating zone (1) and cooling zone (80) comprises one single pressure-resistant container or tank (2'), where the upper part of said container or tank is adapted to act as a hydrate-generating zone (1) while its lower part is adapted to act as a cooling zone (80).

23. A plant according to one of the claims 17-22, c h a r a c t e r i z e d in that each cooling zone (80) is connected to a sluice (60) adapted to transfer the end product to a storage/user/transport-zone (50) having a pressure below the working pressure in the cooling zone (80).

24. A plant according to one of the claims 18-23, characterized in that said means (8,9,35,36) for transferring the first intermediate product from the hydrate-generating zone (1) to the cooling zone (80) comprises a narrow passage (35,36), adapted to limit the transport of the first cooling medium from the hydrate-generating zone (1).

25. A plant according to one of the claims 17-24, characterized in that it comprises means (31,32;97,98;55,56) adapted for mixing and stirring the components in the liquid phase in the hydrate-generating zone (1), in the cooling zone (80), and/or in the storing zone (50).

26. A plant according to one of the claims 17-25, characterized in that the means (87,88) for cooling of the second cooling medium, is adapted to provide a cold, second cooling medium in such an amount and at such a temperature ($T=T_2$) that the hydrate will be cooled down to a temperature ($T=T_0$) at which the hydrate is stable at the ambient air pressure.

27. A plant according to one of the claims 17-26, characterized in that the means for supplying water and the means for supplying the hydrate-forming hydrocarbon, respectively, comprise separate, atomizing nozzles (6,17).

28. A plant according to one of the claims 17-27, characterized in that it comprises

- means adapted for separation of a portion of the first cooling agent from the first intermediate product and/or a portion of the first and the second cooling medium from the end product,
- means adapted for cooling down the separated amounts of cooling agent, and

- means adapted for recirculating the first and/or the second cooling agent, direct cooling of the respective product.

29. A product saturated with hydrocarbon in the form of a hydrate from at least one hydrate-forming hydrocarbon suspended in a hydrocarbon liquid,
c h a r a c t e r i z e d in that the product is a suspension of a solid, hydrate-containing material in a liquid hydrocarbon carrier medium at a storage temperature ($T=T_4$) below the freezing point of water, whereby the liquid hydrocarbon carrier medium has an vapour pressure which at storage temperature is below a storage pressure corresponding to the ambient atmospheric pressure, which product can be manufactured according to a method as stated in claim 1.

30. A product according to claim 29,
c h a r a c t e r i z e d in that the storage temperature is so low that the hydrate is maintained stable at a storage pressure substantially equal to the surrounding pressure.

31. A product according to claim 29 or 30,
c h a r a c t e r i z e d in that the total volume of the solid hydrate-containing material is substantially higher than the total volume of the hydrocarbon carrier medium, preferably equal to or above 70 volume-% of the total volume.

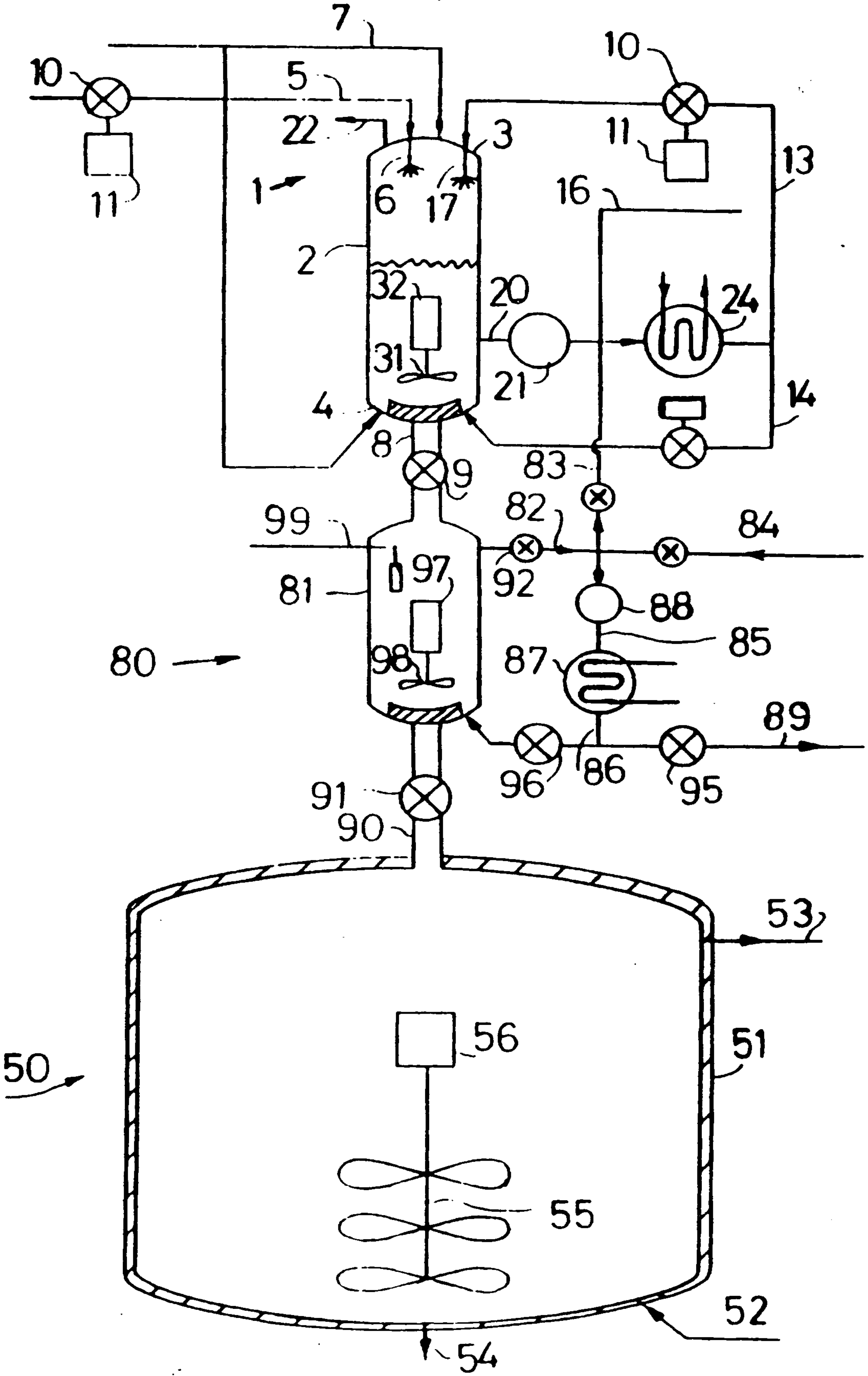
32. A product according to one of the claims 29-31,
c h a r a c t e r i z e d in that the storage temperature is below -7°C, and preferably between -10°C and -35°C, and that the hydrocarbon carrier medium has an vapour pressure which at the storage temperature is below or approximately equals 1 bar.

33. A product according to one of the claims 29-32, characterized in that the solid, hydrate-containing material in the product has a gas content corresponding to a density of at least 130 $Sm^3/m^3$, preferably above 150 $Sm^3$ gas/$m^3$ solids.

34. A product according to one of the claims 29-33, characterized in that the hydrocarbon carrier mainly comprises hydrocarbons having at least 5 carbon atoms in the molecule, preferably a $C_5$- to $C_{10}$-petroleum fraction, and in particular a condensate fraction.

35. A product according to one of the claims 29-34, characterized in that the solid, hydrate-containing material in the product is made up of finely distributed hydrate particles.

36. A method according to one of the claims 1-16, characterized in that the process conditions in step a) are set in such a manner that an end product is obtained in which the solid, hydrate-containing material has a gas content corresponding to a storage density of at least 130 $Sm^3/m^3$, and preferably above 150 $Sm^3/m^3$ solids, when methane is used as the hydrate-forming hydrocarbon.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97
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91
90
53
56
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Fig. 1

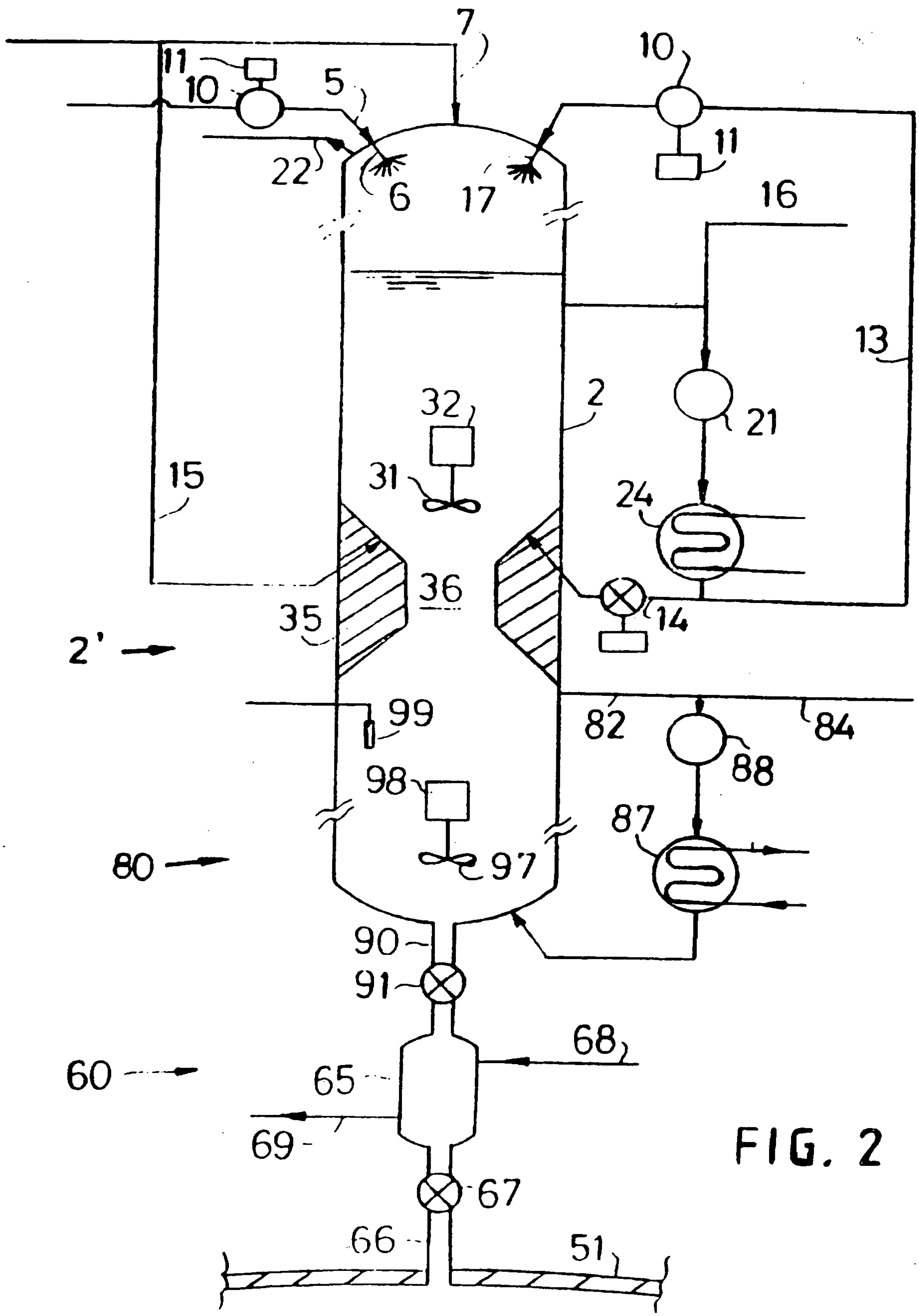
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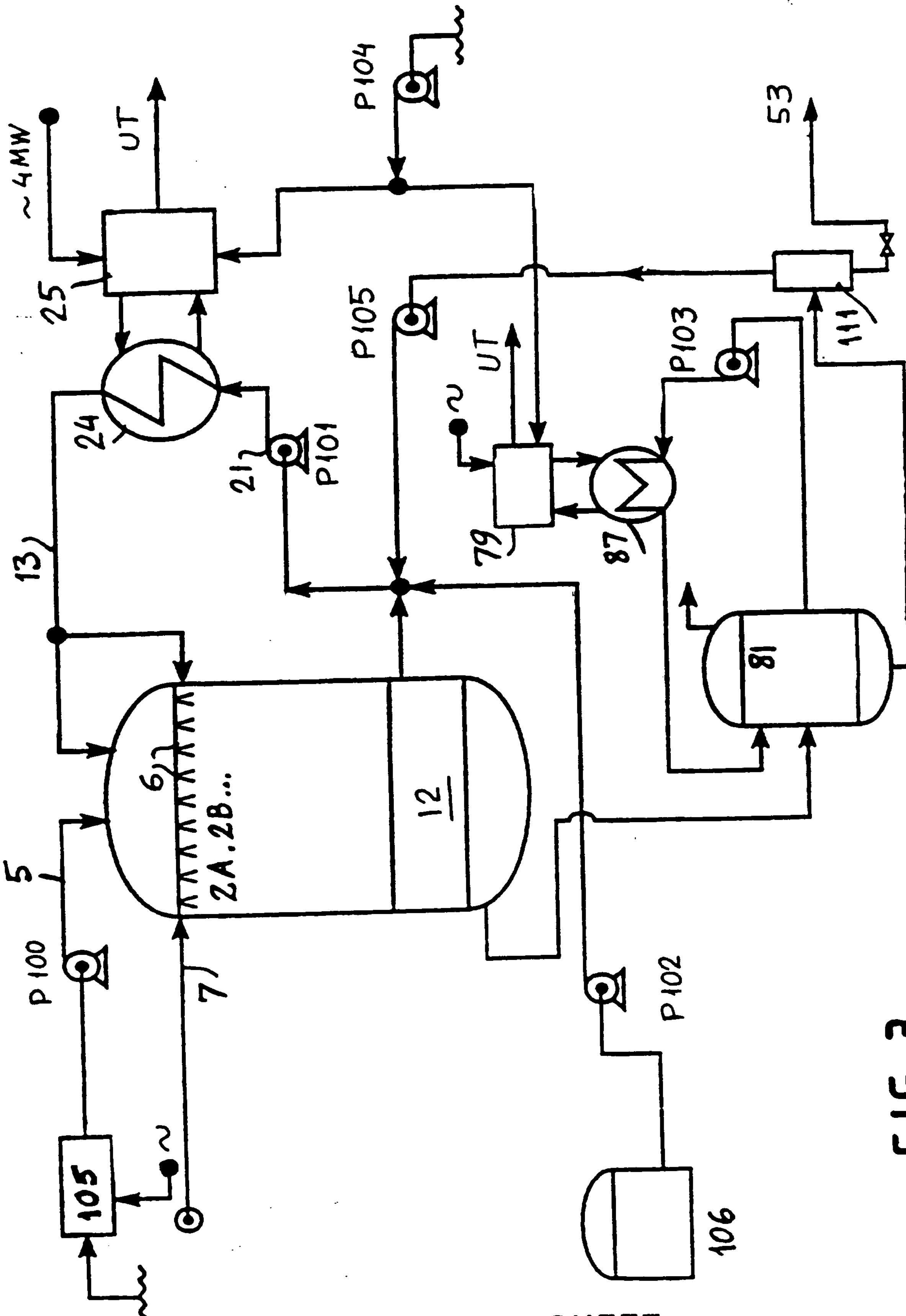
FIG. 2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UT
P104
53
25
P105
P103
UT
111
24
21
P101
79
87
13
81
6
2A, 2B...
12
5
P100
7
P102
105
106

FIG. 3

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 96/00099

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC6: F17C 11/00, F25J 1/02
According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC6: F17C, F25J, B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, CLAIMS

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
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| A | WO 9400713 A1 (DEN NORSKE STATS OLJESELSKAP A.S.), 6 January 1994 (06.01.94)<br>-- | 1-36 |
| A | US 2356407 A (A.J.L. HUTCHINSON), 22 August 1944 (22.08.44)<br>-- | 1-36 |
| A | US 2363529 A (A.J.L. HUTCHINSON), 28 November 1944 (28.11.44)<br>-- | 1-36 |

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:
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"E" erlier document but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
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"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 23 Sept 1996 | 24 -09- 1996 |

| Name and mailing address of the ISA/ | Authorized officer |
|---|---|
| Swedish Patent Office<br>Box 5055, S-102 42 STOCKHOLM<br>Facsimile No. +46 8 666 02 86 | Mårten Hulthén<br>Telephone No. +46 8 782 25 00 |

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 96/00099

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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Information on patent family members

05/09/96

International application No.
PCT/NO 96/00099

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| | | NO-A- 900395 | 30/07/91 |
| | | NO-A- 9000395 | 30/07/91 |
| WO-A1- 9400713 | 06/01/94 | AU-A- 4515393 | 24/01/94 |
| | | EP-A- 0649508 | 26/04/95 |
| | | FI-A- 946165 | 17/02/95 |
| | | NO-B,C- 175656 | 01/08/94 |
| | | NO-A- 922575 | 30/12/93 |
| US-A- 2356407 | 22/08/44 | NONE | |
| US-A- 2363529 | 28/11/44 | NONE | |
| US-A- 3514274 | 26/05/70 | NONE | |

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